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THE INVESTIGATION OF CERTAIN TYPES OF
SOUTH AFRICAN COALS, WITH SPECIAL REF-
ERENCE TO THEIR HIGH NITROGEN CONTENT

By

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY
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INTRODUCTION

The basis of this work is an investigation of certain types of South African coals, planned with a view to obtaining a more fundamental knowledge of the form in which nitrogen exists in coals. Almost all the coals used may be looked upon as high nitrogen coals, five of them containing an average amount of over 2 per cent, as compared with an average of 1 to 1.5 per cent in American coals.

In modern industry the greatest efforts for improvement have been in the direction of a thorough system of utilising by-products. The scientific status of an industry may very often be determined by the way in which it prevents waste in all directions. As an example of this kind the by-product coke industry is no exception. It fails, however, in one respect, namely to recover the maximum amount of nitrogen from the coal.

In the destructive distillation of coal on a large scale, not more than 15 per cent of the nitrogen is obtained as ammonia, while 50 to 60 per cent remains behind in the coke. Attempts to recover this nitrogen from the coke have only succeeded in cases of special treatment, such as the action of steam in the Mond process, or the addition of lime to the coal. In the first of these processes 60 to 70 per cent of

the nitrogen in the coal is obtained as ammonia, and the rest as free nitrogen gas arising from the dissociation of ammonia. But special treatment of this nature destroys the coke and acts detrimentally on other by-products. For this reason it is not always economical. We must, therefore, resort to other means-- to a process which would increase the yield of ammonia without affecting the remaining by-products, and, at the same time keep the total cost more or less constant.

A fundamental study of the nitrogen in coal would add materially to any solution of our problem, and would bring us to a point where further investigation should not be difficult. At the same time a study of the nitrogen would probably throw some light on the constitution of coal-- a subject of great scientific interest and importance.

Importance of the Problem.

Fixed nitrogen in the form of ammonia or ammonium salts or combined with carbon has two main sources through which it finds its way ^{on} to the markets of the world. One of these is from the atmosphere and the other from coal. Today it is uncertain which of these two sources is the more important. Both have their advantages, but the disadvantages of the former-- the heavy initial cost, and the uncertainty

and complexity of the process as a whole-- encourage us to believe, that, for a long time to come, our chief source for ammonia will be from coal. In the United States alone the total reserves of nitrogen in coal are calculated at 31,000,000,000 tons (13).

Explosives and fertilisers-- these two uses alone-- the one largely for the destruction and the other for the maintainance of life-- have made this problem an important one. For the last twenty years or more, We have listened to warnings, that the world is in danger of starvation. However true these warnings may have been, and however well they may have been met by scientific progress, the danger still remains acute. Although there has been a sudden drop in the output of explosives during the last few years, the demand for fixed nitrogen is greater than it has ever been in normal times. This is due to the fact that during the war, much of the nitrogen which should have been used for fertiliser was used for explosives, with the result that the soil suffered and the human food supply decreased by as much as 40 per cent in some European countries. This deficiency has now to be met or the world will soon be underfed. The challenge forms one of the most important and far reaching problems with which the chemist has to deal.

Latest statistics (49) show that the total annual output of ammonium sulphate in the United States from by-product coke industries amounted to 935,000,000 pounds, due to the carbonization of 44,224,000 tons of coal. This quantity of ammonium sulphate is equivalent to 21.2 pounds per ton. Assuming an average of 1.5 per cent of the nitrogen in the coal used, approximately 15 per cent of the nitrogen in the coal was, therefore, recovered. Now if the efficiency of the process could be raised to 100 per cent, an amount of approximately 6,230,000,000 pounds of ammonium sulphate would be obtained from the same amount of coal.

Such a condition would lower the price appreciably and nitrogen fertilisers will be brought within general reach. One of the most pressing problems of modern agriculture would thus be solved.

HISTORICAL

A. On the Nitrogen Content of Coal and The Distribution on Distillation.

As early as 1844 Swindells (1) believing that coke acted as a sort of catalyst in distillation processes, suggested a method of preparing ammonia on a large scale by passing nitrogen, nitric oxides and steam over red hot coke.

Some twenty years later Berthelot (2) tried the preparation of hydrocyanic acid from acetylene and nitrogen in the same way. Seeing that in the distillation of coal quite 50 per cent of the nitrogen remains behind in a form which is decomposed by steam, it is likely that the respective yields obtained in these experiments resulted from this origin.

Henin in 1892 (3) was further attracted by the subject and arrived at conclusions which led Mayer and Altmayer (4) to make a thorough investigation of the effect of steam on the yield of ammonia at different intervals of time between the temperatures of 600° and 900°. They found that a maximum yield of 62.7 per cent of ammonia was obtained at 800°.

A little later James McLeod (5) made an extensive study of the behaviour and distribution of nitrogen in the distillation of coals. He concluded that at the temperature at which the gases are evolved, a part of the nitrogen, which is liberated entirely as free nitrogen, combines with hydrogen to form ammonia, a part with carbon and hydrogen to form cyanogen and pyridine and a part remains as free nitrogen. In distillation experiments in which 227 to 413 tons of coal were utilised, McLeod was able to recover as much as 17 per cent of the nitrogen as ammonia and states that this figure depends on certain factors, such as moisture in, and the physical condition of, the coal. Andrew Short (6) in a later article

summarises a whole series of results obtained in this way, as follows:--

Distribution of nitrogen	Foster	Knoblauch	McLeod	Short
as ammonia	14.5	12.14	17.1	15.16
as cyanogen	1.56	2	1.2	.43
in the coke	48.68	50	58	43.31
in the tar			3.9	2.98
in the gas	35.26	30	19.5	37.12

In 1911 Wolbereck (7) applied these methods using peat instead of coal with a view to obtaining the nitrogen in the form of ammonia.

In 1914 O. Simmersback (8) carried out a series of investigations regarding the relative amounts of ammonia and hydrocyanic acid at temperatures between 800° and 900° and showed the effect of steam on the respective yields. J. W. Cobb in similar experiments found that by removing the ammonia immediately in a distillation process carried out in the laboratory, a yield of 22.5 per cent of the nitrogen could be obtained. He further treated the coke with steam and obtained 60 to 70 per cent of the nitrogen as ammonia-- the conditions found in the Mond process.

In these experiments the ammonia yield rapidly decreases as the temperature rises above 800° C, due to

dissociation of ammonia at these temperatures. Both Simmersback and Cobb conclude that the nitrogen comes off in the form of ammonia, rather than as nitrogen as McLeod suggests.

In 1915 Terres (12) in attempting to determine directly the form in which the nitrogen exists in coal, subjected a number of organic compounds with nitrogen linkages to dry distillation. Such compounds as glycocoll, asparagin, albumin, animal glue, pyridin, azobenzol, hydrazobenzol, ^hpenylisocyanate, nitrobenzol were taken. It was found that only those substances with amino and substituted amino groupings gave ammonia. He, therefore, concludes that the nitrogen has an "albuminous mother substance" for its origin.

In 1920 Glund and Breuer (15) worked on a gas coal of nitrogen content equal to 1.86 per cent and subjected it to low temperature distillation in a revolving cylindrical retort. He found that 66 per cent of the nitrogen remained in the semi-coke and only 1.8 per cent of the nitrogen was liberated as ammonia. When the semi-coke was heated a further 16 per cent was liberated, thus bringing the total yield of ammonia to 17.8 per cent.

In an unpublished thesis (16a) by Chiles (1920) the author attempted to determine actually what changes occur in the nitrogen molecule during the coking of coal. Attempts were made to prepare synthetically the same compound as it

exists in coal by fusing chemically pure carbon obtained from sugar and protein substances. No definite conclusions were drawn, but results seemed to indicate the presence of nitrides, or direct combination of carbon and nitrogen.

In 1921 Monkhouse and Cobb (16) determined the effect of hydrogen and nitrogen alone, and in the presence of steam, on coke residues prepared at 500°, 800°, and 1100° C, 34.24 per cent of the nitrogen of the coke was obtained with 500° C coke using hydrogen gas. This was the highest yield obtained.

B. On the Constitution of Coal.

Running almost parallel with these results is to be found a series of researches carried on with a view to obtaining a more fundamental idea of the constitution of coal. A determination of the form of nitrogen in coal would be a step in this direction. For this reason these researches have been described.

In this work three general methods have been universally employed, (1) that of selective solvents (2) microscopic investigations and (3) distillation processes.

The first work on the use of solvents seems to have been done by Dr Smythe (21) at Gottingen, and was published in a report to the commissioners of the 1851 exhibition. He used a Cologne coal and classified the following solvents in order of their extractive ability:-- benzene 3 per cent

chloroform 1.8 per cent, ethyl alcohol 2.4 per cent, ether, petroleum ether and acetone--the latter three dissolving out a very small portion of the coal. In all these extracts, except that from alcohol, nitrogen is reported absent.

In 1879 Guignet (17) tried the action of phenol on coal, and extracted 4 per cent of the coal. He then tried the action of nitric acid on the residue and extract. This work was followed up by Friswell (18), who compared the action of nitric acid on graphite and coal respectively. With coal he obtained a crystalline product which he believed to be a nitro compound, similar to nitrocellulose. From 90 grams of a bituminous coal, finely ground, a residue of 12.5 grams was obtained.

About the same time Smith (19) in trying the action of benzene on coal, found that with a certain Japanese coal an extract as high as 10 per cent was obtained. Smith points out the unique nature of this coal, and goes a step further in a theory, in which he compares the origin of coal with that of petroleum. He suggests that the anthracite coal of Pennsylvania was probably at one time of its formation a bituminous coal similar to the one of Japan on which he worked, but owing to pressure, temperature and other physical phenomena, had been deprived of its bitumin which nowadays is being brought to the surface in the form of petroleum. Regarding the nitrogen

in the coal, Smith seems to think that a high nitrogen content should predict animal origin and substantiates his theory by comparing the nitrogen content of tar from wood and from bone respectively.

Following these experiments work of Dr. Smythe (21) is again referred to, in which he attacked coal with dilute hydrochloric acid and potassium chlorate. Thirty to 35 per cent of the coal was then found to be soluble in alcohol and acetone. By extraction with benzene he was able to separate a number of substances containing chlorine and a high percentage of oxygen. Thus $C_{30}H_{22}Cl_8O_{10}$ and $C_{35}H_{36}Cl_4O_{20}$ were recognised. Anderson and Roberts (22) took up the work from here and extracted an El coal, which had been previously oxidised by atmosphere oxygen and by dilute HNO_3 , with potassium hydroxide. They were able by this means to extract a number of acid substances believed to be derivatives of humic acid. Finally they conclude that the nitrogen, or nitrogen containing substances, in the coal have absolutely nothing to do with the coking properties of the coal. They believe that the coking property of coal is due to the ease with which certain substances in the coal will volatilize or decompose, and that a considerable portion of the organic matter in coal consists of a complex compound comparatively rich in nitrogen, and containing sulphur as well. In addition to these, resinous material is always present to a small, but fairly constant,

extent. They state that "the nitrogenous bodies obviously owe their origin to the proteid substances of the vegetable matter from which the coal was formed".

Donath and Margosches (24) added powdered permanganate to their alkali solvent and arrived at results which strengthened the view that when oxidised, coal yields acid substances, resembling humic acids..

In 1901 Baker (23) tried the action of pyridin on coal. Donath (25) a little later carried the study further on a German coal. These results were followed by a series of experiments by Bedson (26) on gas coals. Twenty-four to 35 per cent of pyridin soluble material was obtained. He suggested that the pyridin extract might be related to the volatile matter in the coal, but this theory was afterwards disproved. He also applied different organic solvents to extracts and residue and obtained interesting results, though no definite conclusions.

In 1911 Lewes (28) continued the work and arrived at interesting conclusions regarding the coking properties of the residue and extract. He explains the retention of the coking properties of some coals by assuming the presence of a resinic body not soluble in pyridin. He further noticed that the percentage of volatile matter of certain coals had increased after extraction and concluded that some of the pyridin was held back by the coal to form a compound with the insoluble

part. Lewes points out that pyridin is, therefore, an unsuitable solvent, especially for nitrogen investigations. He further states that the resinous bodies in coal are of two kinds "the one easily oxidisable, soluble in pyridin and saponifiable by alkalies, and which on weathering is oxidised into humus bodies with the evolution of water and carbon dioxide, and the other non oxidisable, not saponified by alkalies, and forming with pyridin a compound insoluble in excess of the reagent; and this class may be the hydro-carbons from decomposed resins, as the residue in which they are present yields rich liquid hydro-carbons, as tar and pitch, but not rich in gas."

In 1911 Pictet (29) working at different times in conjunctions with Ramseier, Bouvier, Labonchere, Combes and Kaiser, started on a series of researches which gradually developed into a very interesting, as well as a useful piece of work. These investigators attacked the problem from two angles. In their first series of experiments they extracted a "fat" coal of Montrambert (Loire) with benzene. The distillate was obtained in the form of a tar, which was fractionally distilled into a number of products, which the authors were able to identify. Amongst these compounds were hexahydrofluorene, a number of hydro-carbons, phenols and bases. The same coal was then subjected to vacuum distillation up to a temperature of 450° and at a pressure of 13 to 15 mm. The tar obtained was

found to be similar to the tar obtained in the first case, and these in turn showed marked resemblances to the fractions obtained from petroleum. The authors finally conclude that the coal and petroleum have similar origins (41). These investigations were started with the object of finding out the form in which nitrogen exists in coal, but no conclusions on this point were drawn.

About the same time that these researches were begun, Wheeler together with Burgess (30), Jones (35) and Clarke (33) set out on a thorough investigation on the solvent action of pyridin on coal and were able to arrive at conclusions on which a theory was based. They found that when coal was extracted with pyridin, the extract contained resinous decomposition products together with a substance of cellulosic origin. These two substances they were able to separate by means of chloroform. On destructive distillation of these three substances they found that the residue yielded chiefly hydrogen, while the pyridin soluble, chloroform insoluble part, yielded chiefly hydro-carbons. The chloroform soluble part of the extract resembled the residue in yielding chiefly hydrogen. They therefore concluded that coal was composed of two parts (1) the hydrogen yielding and (2) the paraffin yielding constituents. They further illustrated their results by analysing the gases given off at different temperatures in the destructive distillation of coal.

In 1912 Hoffman and Fraser (31) published a paper on "The Constituents of Coal Soluble in Phenol". Illinois coal from Franklin County was taken and it was found that 10.87 per cent calculated on the moisture and ash free basis was soluble. By the use of sodium hydroxide and other organic solvents they were able to extract certain substances out of the coal which they believed to be pure. Complete analysis of these substances were given, but no constitutional formula established.

This work was followed up by Parr and Hadley (34) in a very thorough investigation on the properties of the residue and extract, using phenol as solvent. These investigators believe that phenol is the best solvent to use as it undergoes decomposition only to a very slight degree and does not effect the coal as does pyridin. Both the residue and extract were analysed and examined in regard to their resistance to air and their coking properties. They find that the nitrogen divides itself more or less evenly between the residue and extract.

Porter and Taylor (36), working on the volatile products of coal, carried out investigations on four coals, which unfortunately had been weathered. They arrived at results on the constitution of coal which were opposed to those of Wheeler and state that the "cellulosic" material in the coal is first decomposed on exposure to heat.

Microscopically some very brilliant researches have

been carried out on coal, which throw a good deal of light on its origin and constitution. Amongst the foremost workers in this field may be mentioned Thiessen (39), White (38), Stopes and Wheeler (37).

In the last four or five years a great deal of investigation has been done on the action of chemical reagents on coal which has produced interesting though not conclusive results. This work has mostly originated from German chemists, and unfortunately could not be obtained in the original articles by the writer.

Thus Keller, Hilpert and Lepsius (40) treated a bituminous coal with acetic anhydride and zinc chloride in a sealed tube and then subjected the residue with nitric acid. The content of nitrogen increased from 1.8 per cent to 8 per cent. This substance they called "nitro-coal". They found it insoluble in acetone, acetic acid and benzene. The extract resembled the residue when these were subjected to destructive distillation, and was soluble in alkalies. They failed to prepare sulphuric acid derivatives and suggested the absence of aromatic hydrocarbons as a result.

Fisher and Groppel (41) about the same time tried the effect of pre-heating the coal and thereby increasing the extracts obtained by solvents.

With Niggeman (42), Fisher tried the effect of ozone

on coal, and found that the humic acid substances were rendered soluble--the amount being inversely proportional to the coking properties of the coal. The ozonised product was dried at 110° and contained 3 per cent H, 50 per cent C, .8 per cent S and only traces of nitrogen--the original coal containing 5 per cent H, 84 per cent C, .9 per cent S. A little later Fisher and Tropsch (47) tried the same reaction in a non aqueous media, but could observe no changes in the reaction. The same authors also tried the effect of hydrogen iodide (47) on coal and found that coals of early origin were attacked sooner than those of later origin. The amount of extract obtained with chloroform after such treatment was increased from 2.7 per cent to 73 per cent in the case of a camel coal.

In 1921 F. Fischer and Schrader (48) published a paper on the origin and chemical structure of coal, which contained a number of new ideas and new theories, not the least of which was the fact that they question all previous theories on the subject. According to them coal originates from the lignin in the plant --the cellulose being decomposed by bacterial action in the early stages of peat formation, with the formation of CO_2 and H_2O . Lignin, they state, has an aromatic structure, with acetyl and methoxyl groups. Thus in the formation of peat the methoxyl groups increase, while the portion soluble in concentrated hydrochloric acid decreases. Finally the methoxyl

groups are replaced by hydroxyl groups to form a compound identical with humic acid. Further splitting off of H_2O , CO_2 and CH_4 give rise to lignite. The authors quote experimental evidence in proof of their theory.

Five months later a further article appeared in which the above theory received severe criticism at the hands of Klever, Forschner, Jonas and others. The question still remains unsettled.

The Coals Studied.

The coals which formed the basis of the study described in this paper came from South Africa. Fourteen samples from different mines were sent to this University by Mr. P. Wagener, Inspector of Mines for the Union of South Africa. These samples were taken according to standard methods and were received in good condition in well sealed tins. Unfortunately all but a few were packed in the finely ground condition--a condition in which weathering is most effective. No attempts were made to investigate the extent of weathering.

The coal resources of the Union of South Africa were estimated in 1913 at 57,839 million tons. This is probably a considerable underestimate. Between 1913 and 1920 the total output of the Union was increased by 45 per cent, it being nearly 12 million tons for 1920.

Almost all the coal in the Union comes from two states, the Transvaal and Natal--the latter coals being of a slightly higher quality. The position of these fields is shown in the map in(Figure I), according to the following list.

1. Utrecht Collieries--Natal
2. Cambria Collieries--Dannhouse Natal
3. South African Northfield Collieries--Glencoe Natal
4. Navigation Collieries--Natal
5. Transvaal and Delegoa Bay--Witbank
6. Clydesdale Collieries
7. Cassel Coal Coy--Blackhill
8. Middelburg Steam Coal & Coke Coy
9. Coronation Collieries
10. Emyati Collieries--Langk^rans--Natal
11. Uitspan Collieries--Witbank
12. Clydesdale Collieries
13. Tavistock Coal and Coke Co--Witbank
14. African Freehold Coal Lands Ltd.
Vaalbank, Middelburg

Experimental.

In order to get a thorough idea of the nature of these coals complete analyses were made. The methods used were those described in "Gas and Fuel Analysis" by White, "Water and Fuel Analysis" by Parr and "Methods of Analysing Coal and Coke" by Stanton and Fildner.

Total carbon was determined by the Parr "total carbon" apparatus. Oxygen and hydrogen were calculated from the Dulong formula. Heat values were made by the Parr Adiabatic Calorimeter.

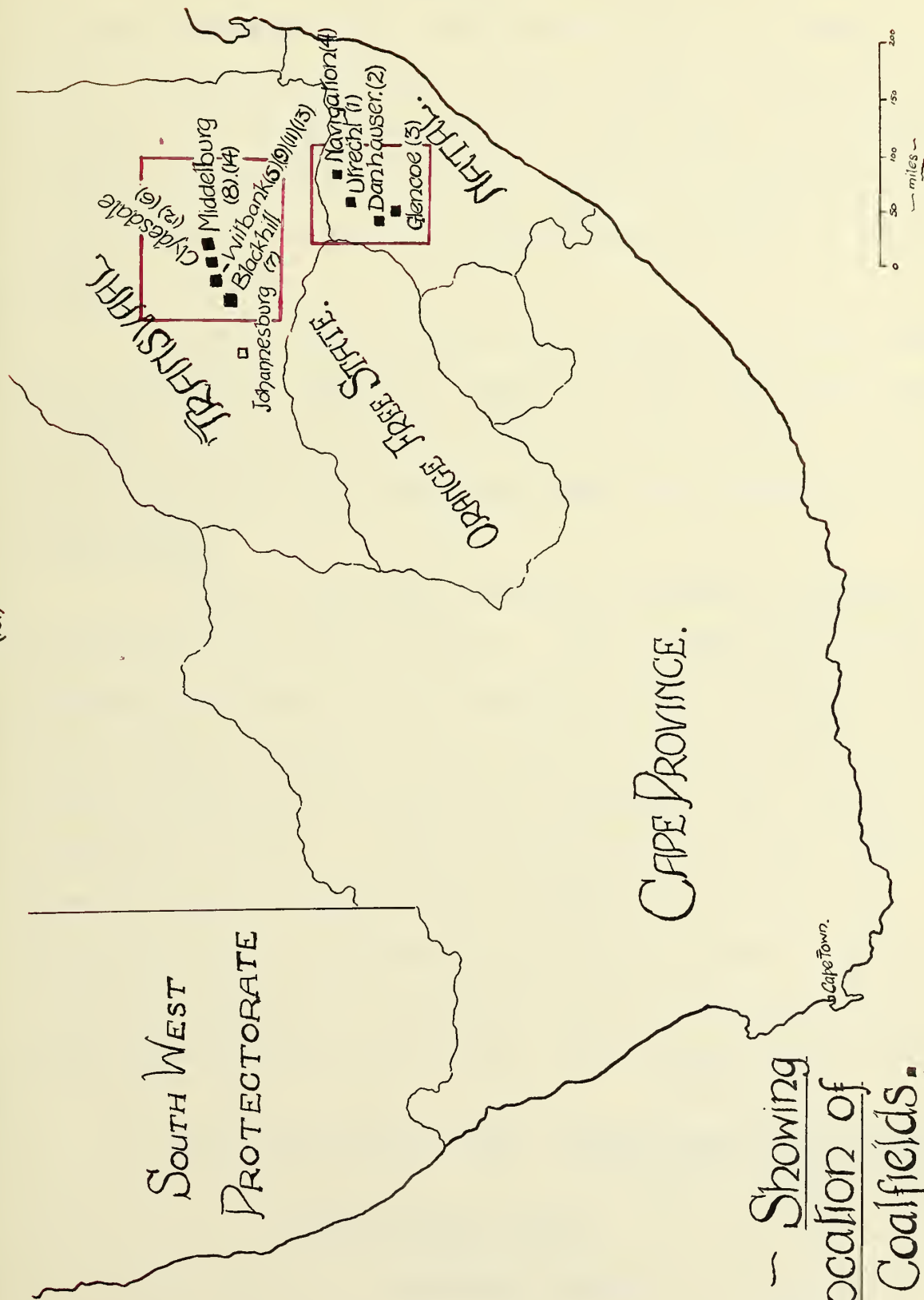


Fig1 - Showing
location of
Coalfields.

The Kjeldahl Gunning method was employed in all nitrogen determinations. One gramme of coal is placed in a 500 cc Kjeldahl flask, and .5 grams of KHSO_4 , .5 grams of Hg. and 30 cc of concentrated sulphuric acid added. The mixture is digested for three to four hours and after removing the Hg with K_2S is finally distilled in the presence of NaOH into standard H_2SO_4 .

In the case of coke it is advisable to take .5 grams of the material, digest for three hours then add a few crystals of KMnO_4 and finally digest for three hours longer. In each set of determinations blanks were made and subtracted from the total amount.

Table 1 shows the proximate analyses, calculated to the moisture and ash free basis; Table 2 shows the ultimate analyses and Table 3 their classification. In order to get a better understanding of their classification, each coal was plotted graphically (Figure II) according to the classification of Parr and Vliet. In this classification the unit volatile matter is plotted against the unit Btu value of the coal. Unit volatile matter is defined as the volatile matter on the pure coal substance and is calculated from the following formulas.

unit volatile matter (pure coal) = $100 - \text{fixed carbon on pure coal basis}$

$$\text{fixed carbon (pure coal)} = \frac{\text{fixed carbon as determined}}{1 - (1.08 A - 1/2S - 1/20S - M)}$$

where A=ash content.

S=sulphur content

M=moisture content

TABLE I

SHOWING PROXIMATE ANALYSIS OF COALS

(21)

Locality	Laboratory Number	Proximate ANALYSIS		Moisture free		Moisture & Ash Free		air drying loss
		H ₂ O	Vol fixed mat carbon	Ash	Vol fixed mat carbon	Ash	Vol fixed mat carbon	
Utrecht Natal	1	2.83	25.93	60.64	10.60	26.69	62.40	.22
Cambria Coll Natal	2	1.42	28.04	62.28	8.26	28.44	63.18	.23
S.A. Northfield Coll. Natal	3	1.53	23.10	68.02	7.35	23.46	69.08	.17
Navigation Coll Natal	4	1.47	22.29	67.14	9.10	22.60	68.16	.21
Transvaal & Delegoa Bay Witbank (8)	5	1.88	33.41	51.85	12.86	39.04	52.85	.36
Clydesdale Coll. Blackhill No. 2	6	2.60	28.28	57.93	11.19	29.02	59.50	.12
Cassel Coal Coy Blackhill No. 1	7	1.93	29.98	57.61	10.48	30.58	58.73	.13
Steam Coal & Coke Middleburg	8	1.94	27.99	54.09	15.98	28.54	55.17	.23
Coronation Coll No. 3	9	1.87	27.56	57.24	13.33	28.08	58.34	.16
Emyati Coll Natal	10	1.28	23.70	67.06	7.96	24.01	67.95	.31
Uitspan Coll Witbank No. 10	11	1.81	25.47	58.07	14.65	25.93	59.15	.11
Clydesdale Coll No. 2	12	2.48	28.46	57.44	11.62	29.18	58.90	.19
Tavistock Coal & Coke Coy No. 6	13	2.03	28.43	58.46	11.08	29.02	59.67	.27
African Free- hold Coal & Coke Coy (11)	14	2.57	29.16	57.68	10.59	29.93	59.21	.32

Table 2

SHOWING ULTIMATE ANALYSIS OF COALS

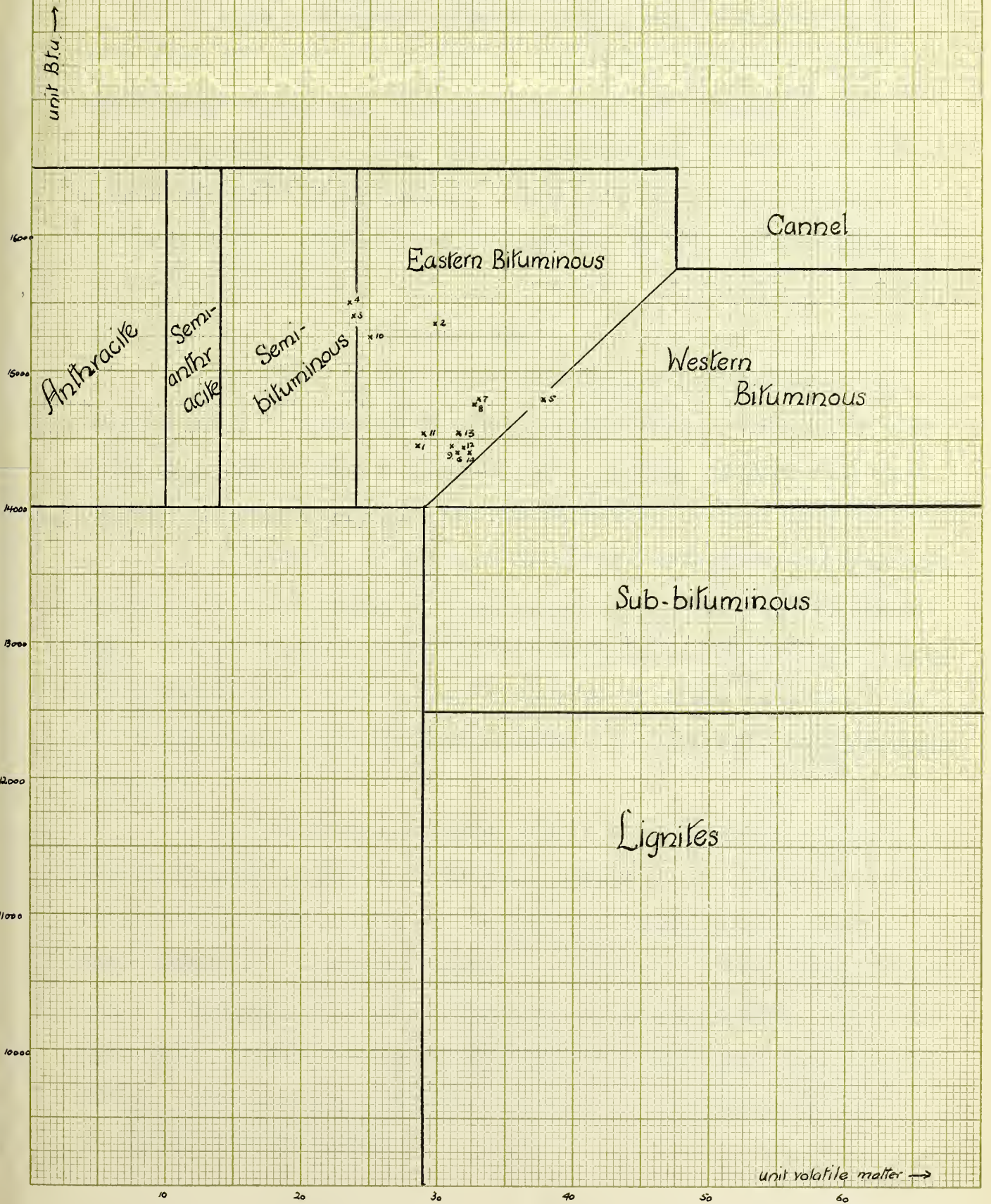
Location	Laboratory Number	Ultimate Analysis					Calorific Value	
		S.	H ₂	Carbon	N ₂	O ₂	Calories	B.t.u
Utrecht Coll. Natal	1	1.58	4.45	70.70	2.12	7.72	6952	12534
Cambria Coll. Natal	2	1.67	4.90	75.93	2.17	5.66	7616	13707
S.A. Northfield Coll. Natal	3	1.71	4.79	77.33	2.32	4.97	7726	13917
Navigation Coll. Natal	4	1.72	4.64	76.30	2.17	4.60	7606	13695
Transvaal & Delegea Bay. Witbank No. 8	5	1.24	4.81	69.33	1.68	8.20	6900	12421
Clydesdale Coll. Blackhill No. 2	6	1.26	4.22	70.50	1.62	8.61	6808	12255
Cassel Coal Coy Blackhill No. 1	7	1.29	4.46	71.98	1.68	8.18	7057	12702
Steam Coal & Coke Middleburg	8	.87	4.16	67.45	1.53	8.07	6558	11805
Coronation Coll. No. 3	9	.88	4.80	68.18	1.67	9.27	6787	12119
Emyati Coll. Natal	10	1.24	4.54	77.47	2.11	5.40	7622	13720
Uitspan Coll. Witbank No. 10	11	.84	4.23	68.43	1.61	8.43	6645	11960
Clydesdale No. 2	12	1.40	4.33	69.86	1.60	8.61	6797	12232
Tavistock Coal Coy Witbank No. 6	13	1.39	4.30	71.38	1.75	8.07	6925	12464
African Freehold Middleburg No. 11	14	.42	4.54	70.38	1.78	9.72	6885	12392

Table 3

SHOWING THE CLASSIFICATION

Locality	Lab'y No.	Vol.Mat. (air dried)	Unit B.t.u.	Vol.Mat. on Unit coal.
Cambria Coll. Natal	2	28.04	15351	29.80
Emyati Coll. Natal	10	23.70	15271	25.01
S.A.Northfield Coll. Natal	3	23.10	15421	24.07
Navigation Coll. Natal	4	22.29	15508	23.50
Transvaal & Delegoa Bay. Witbank No. 8	5	33.41	14805	37.96
Cassel Coal Coy Blackhill No. 1	7	29.98	14803	33.05
Steam Coal & Coke Middleburg	8	27.99	14767	32.65
Clydesdale Coll. Blackhill No. 2	6	28.28	14409	31.55
Coronation Coll. No. 3	9	27.56	14426	31.24
Clydesdale No. 2	12	28.46	14444	31.88
African Freehold Coal Coy. Middle- burg No. 11	14	29.16	14425	32.45
Utrecht Coll. Natal	1	25.93	14442	28.53
Uitspan Coll. Witbank No. 10	11	25.47	14550	29.13
Tavistock Coal Coy Witbank No. 6	13	28.43	14541	31.47

— Fig 2 - Showing classification of coals —



The Nitrogen in the Coal.

From this point attempts were made to determine in what form the nitrogen exists in coal. For this purpose two methods of attack were adopted (1) the distillation of coal in the presence of carbon dioxide (2) the use of chemical reagents at lower temperatures. According to a recent thesis by Hobwart (57) carbon dioxide does not affect carbonization processes in any way.

Theoretical

In order to get some basis upon which to build, it is necessary to make use of certain theoretical considerations regarding the origin of coal--theories which, however, are now widely accepted by geologists and chemists.

Thus David White (38) in a very extensive and thorough bulletin on "The Origin of Coal", and later Thiessen and White (39) on the "Structure in Paleozoic Bituminous Coals" claim that the decomposition towards the formation of coal, is exposed to two fundamental agencies (1) Biochemical or Bacterial and (2) Dynamiochemical.

In the first of these stages the formation of peat, or its equivalent in rank, is brought about; in the latter the peat is exposed to the action of pressure and temperature, during which process a low grade lignite is formed. Water is expressed, thereby reducing the mass by as much as three-fourths, gases are expelled, organic compounds are further broken down and finally oxygen, nitrogen and hydrogen, together with varying amounts of carbon are liberated..

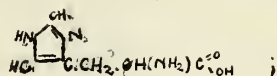
Furthermore at this stage we assume that the nitrogen in coal originates from the protein at one time present in the plant from which the coal was formed. Coming from the plant it is certain that the nitrogen is of organic and not of inorganic origin. It is true that certain plants contain alkaloids, in which the nitrogen is bound differently in the molecule from protein, but it is not likely that these compounds play any part in coal formation, for such plants are not common and are small in bulk. All writers who have had anything to do with the nitrogen in coal have believed that protein is its true origin.

Proteins in the presence of hydrolysing agents such as dilute hydrochloric acid, readily decompose. This has been shown by Hlasiwetz and Haberman (50), Kossel (51), Kutscher (52), Emil Fischer (53) and others. Thus when proteins are hydrolysed in the laboratory we obtain chiefly as decomposition products the following groups of compounds:

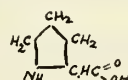
(1) Amino acids, which include monamino and diamino carboxylic acids, eg: Amino acetic, amino valeric, diamino propionic, diamino glutamic.

(2) Acid amides eg: acetamide.

(3) Heterocyclic compounds eg: Histidine, having the formula



proline



and oxyproline.

Now when proteins are exposed to the natural agencies as are supposed to exist in the formation of coal, we would expect hydrolysis brought about by bacterial action, and as a result, the products of decomposition would be brought down in

the coal. There is, however, a possibility for chemical combination to take place with other organic compounds in the plant before complete hydrolysis has taken place, especially if the protein is protected in some physical way by the plant tissue. This possibility is dealt with in later experiments which determine the effect of hydroly^{sing}/agents on the nitrogen molecule in coal. These theoretical considerations form the basis of the work which is to follow.

Experimental.

A. Distillation.

In the first series of experiments a thorough investigation was made of the behaviour of the nitrogen when coal is distilled in an atmosphere of carbon dioxide, between the temperatures of 450° and 600° C. These temperatures were chosen because it was found that below 450° C the quantities of tar and ammonia which could be collected from 100 grams of coal were hardly sufficient to enable us to make any determinations. On the other hand at 600° C the gases could be removed before any appreciable decomposition of the ammonia or tar takes place.

In the distillation of coal it is universally known that the respective yields of coke, tar and gas depend upon the conditions of the process. Such factors, for instance, as temperature, pressure, time and contact surfaces will alter the yields in appreciable amounts. Consequently all attempts were made to keep other factors, beside the temperature, constant in different experiments.

For this purpose the apparatus was used as is shown in

the diagram (Fig. 3) 100 grams of coal in the finely ground condition were placed in A for each run. By lowering F as much of the air is withdrawn from the apparatus as possible. Carbon dioxide is then passed through the apparatus through the tube C for one-half to three quarters of an hour. The heating is done ~~electrically~~ electrically and the temperature kept constant during each run by a series of resistances. As temperature and time are important factors in distillation processes, the rate of heating of the furnace is shown in (Fig. 4).

The tar collects in B, and the gases, after being filtered through glass wool in C, pass through the two flasks D, each containing about 100 cc of approximately normal sulphuric acid. Finally the gas is collected in E under reduced pressure obtained by lowering F to the same extent in each case.

Four coals are heated in this way. In each case gases begin to come off as soon as the temperature begins to rise. This steady evolution of gas continues throughout the experiment and at about 400° C, a further decomposition in the coal is shown in the appearance of tar. The coal is subjected to each temperature for periods of five hours.

The ammonia given off is collected very efficiently in the two conical flasks D of 150 cc capacity. The contents of the flasks are finally transferred to a measuring flask and made up to 200 cc. Aliquot parts are distilled in the presence of sodium hydroxide into standard acid and the amount of ammonia thus calculated.

The tar and water given off are collected in B. A

separation of these products is brought about by the centrifuge and the respective quantities measured.

Analyses of the gases given off in each case showed small percentages of nitrogen. These amounts evidently arose, partly from the occluded gases which are always present in coals and partly from the decomposition of ammonia. The amounts were small and consequently neglected in the calculations.

The results are shown in tables 4 to 11. In tables 12 to 15, the percentage distribution of nitrogen is given at each temperature. In these cases the error, that is the percentage of nitrogen unaccounted for, is given. In cases where the error is indicated by a positive sign, it appears that the sum total per cent of nitrogen in the coke, tar and ammonia is more than in the original coal. In other cases indicated by the minus sign, some of the nitrogen still remains unaccounted for. The discrepancy may be due to inconsistencies in the Kjeldahl-gunning method for determining nitrogen in coke. Some of these errors are greater than experimental error would warrant. Yet considering that the quantities of coal and coke are taken to the nearest gramme, on the whole the results agree remarkably well, and give us a very excellent idea of what happens to the nitrogen part of the molecule when coal is distilled between these temperatures.

These results are explained in another way in the diagrams shown in Figures 5 to 13. Here we have endeavored to show the behaviour of each coal separately as it passes from one temperature to another. Thus Figures 5 to 8 show the respective amounts of volatile matter, tar, ammonia and gas of each coal at

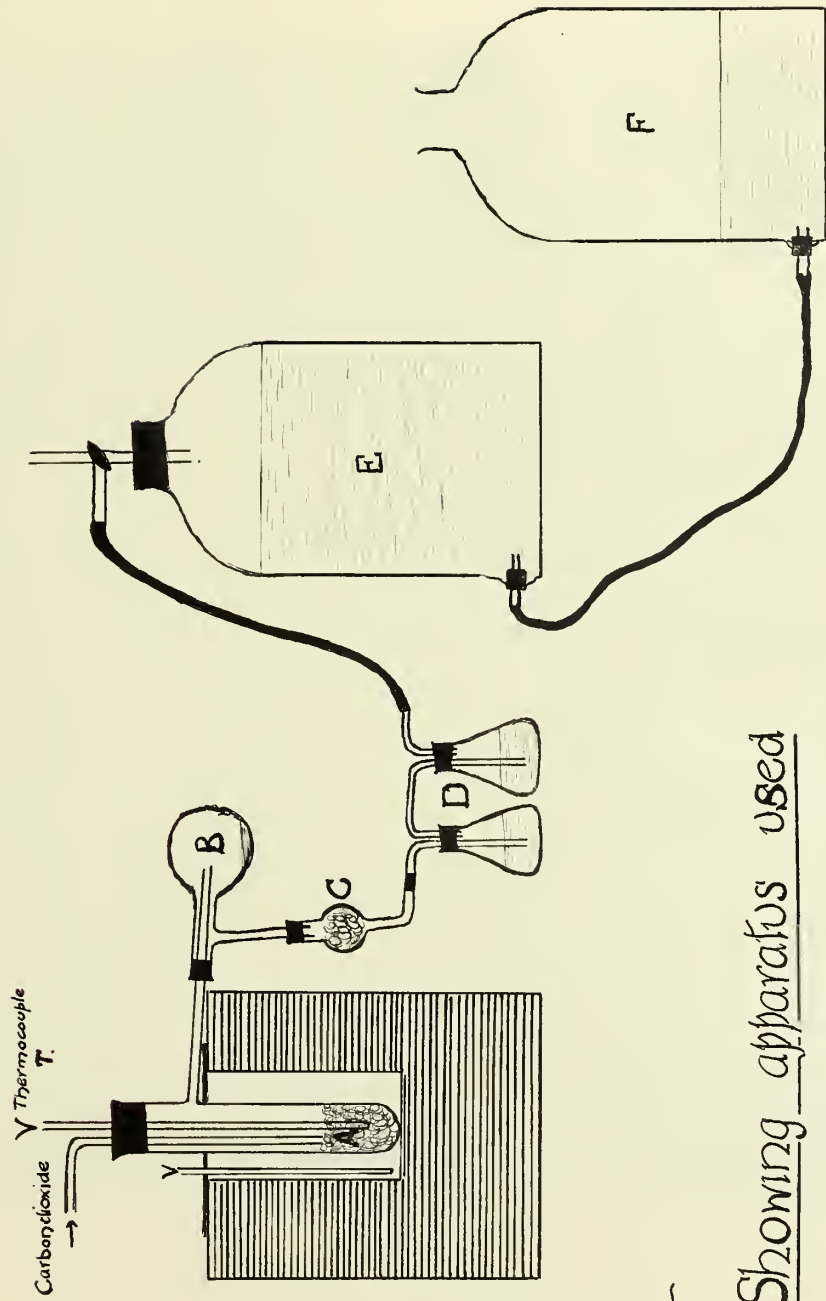


Fig. 3. -
Showing apparatus used
for distillation experiments.

Fig. 4

SHOWING FURNACE RISE IN TEMPERATURE WITH TIME.

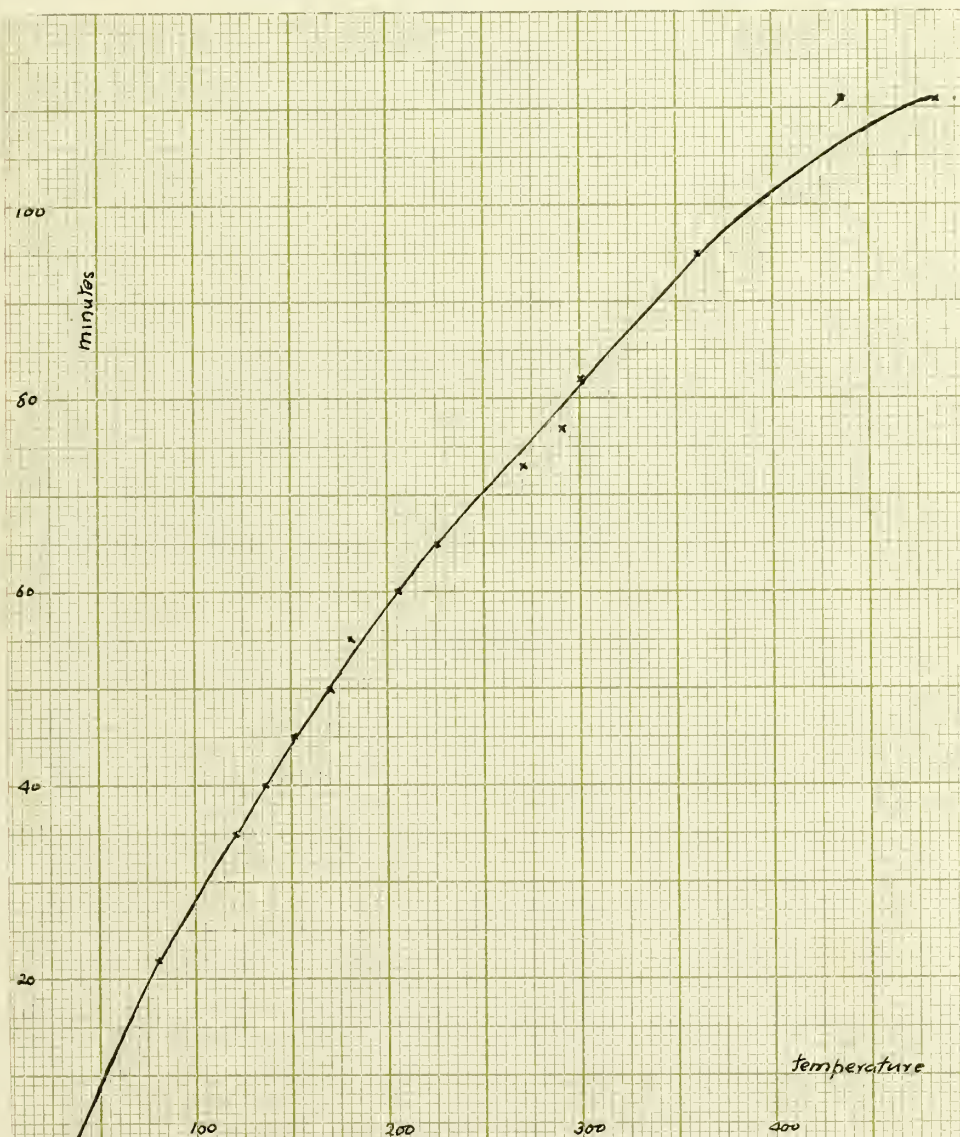


Table 4

SHOWING ACTUAL QUANTITIES GIVEN OFF AT 450° C

Experiment Number	Amount of coal taken (gms)	Coke	Tar	NH ₃	Gas	H ₂ O
3 A	100	88	3.23	.0085	6325	3.3
7 B	100	83	5	0070	6150	4.0
11 C	100	87	3.3	0081	5400	4.5
14 D	100	83	3.10	0010	5700	6.00

Table 5

SHOWING ACTUAL QUANTITIES GIVEN OFF AT 500° C

Experiment Number	Amount of coal taken	Coke	Tar	NH ₃	Gas	H ₂ O
3 E	100	87	3.90	.011	8900	3.5
7 F	100	81	5.6	0075	8400	5.8
11 G	100	86	3.53	0087	7200	5.8
14 H	100	79	6.00	0021	8000	7

Table 6

SHOWING ACTUAL QUANTITIES GIVEN OFF AT 550° C

Experiment Number	Amount of coal taken (gms)	Coke	Tar	NH ₃	Gas	H ₂ O
3 I	100	84	3.92	.054	12900	3.5
7 J	100	79	5.7	.016	9950	6
11 K	100	84	3.80	.0088	8450	6
14 L	100	78	6.30	.016	9400	7

Table 7

SHOWING ACTUAL QUANTITIES GIVEN OFF AT 600° C

Experiment Number	Amount of coal taken (gms)	Coke	Tar	NH ₃	Gas	H ₂ O
3 M	100	82.5	4.10	056	15000	4.5
7 N	100	77	5.7	034	11900	6
11 O	100	81	3.82	023	10600	6
14 P	100	76	6.46	043	11650	7

Table 8

SHOWING PERCENTAGE OF NITROGEN IN PRODUCTS GIVEN
OFF AT 450° C

Experiment Number	Coal	Coke	Tar	NH ₃	Gas
3 A	2.32	2.70	.85	0067	-
7 B	1.68	2.03	.95	0058	1.5
11 C	1.61	1.85	.92	0067	2.8
14 D	1.78	2.07	.60	0008	1.9

Table 9

SHOWING PERCENTAGE OF NITROGEN IN PRODUCTS GIVEN
OFF AT 500° C

Experiment Number	Coal	Coke	Tar	NH ₃	Gas
3 E	2.32	2.68	.95	.009	2.5
7 F	1.68	1.89	.99	0062	4
11 G	1.61	1.80	.97	0072	2.8
14 H	1.78	2.07	.92	0017	2.3

Table 10

SHOWING PERCENTAGE OF NITROGEN IN PRODUCTS GIVEN
OFF AT 550° C

Experiment Number	Coal	Coke	Tar	NH ₃	Gas
3 I	2.32	2.67	1.10	045	-
7 J	1.68	1.93	1.00	014	2.8
11 K	1.61	1.84	1.09	0073	2.8
14 L	1.78	2.10	.98	014	1.10

Table 11

SHOWING PERCENTAGE NITROGEN IN PRODUCTS GIVEN
OFF AT 600° C

Experiment Number	Coal	Coke	Tar	NH ₃	Gas
3 M	2.32	2.70	1.10	046	4
7 N	1.68	1.91	1.00	028	3.10
11 O	1.61	1.78	1.10	019	2.8
14 P	1.78	2.12	.99	035	4.80

Table 12

-36-

SHOWING PERCENTAGE DISTRIBUTION OF NITROGEN AT 450° C

	3		7		11		14	
	%	% distrib.	%	% distrib.	%	% distrib.	%	% distrib.
Coke	2.38	98.60	1.68	96.94	1.61	97.75	1.72	98.85
Tar	.027	1.12	.047	2.71	.03	1.82	.019	1.09
NH ₃	.0067	.27	.0058	.34	.0067	.41	.0008	.05
Error		+09		+.05		+.034		-.04

Table 13SHOWING PERCENTAGE DISTRIBUTION OF NITROGEN AT 500° C

	3		7		11		14	
	%	% distrib.	%	% distrib.	%	% distrib.	%	% distrib.
Coke	2.34	98.07	1.53	96.23	1.55	97.48	1.64	96.47
Tar	.037	1.80	.055	3.46	.034	2.14	.055	3.23
NH ₃	.009	.38	.0062	.39	.0072	.45	.0017	.10
Error		+.07		-.09		-.02		-.08

Table 14

SHOWING PERCENTAGE DISTRIBUTION OF NITROGEN AT 550° C

	3		7		11		14	
	%	%distrib.	%	%distrib.	%	% distrib	%	%distrib.
Coke	2.24	96.13	1.53	95.62	1.55	96.88	1.64	95.57
Tar	.043	1.84	.057	3.55	.041	2.56	.062	3.61
NH ₃	.045	1.93	.016	.9	.0073	.46	.014	.82
Error		+.01		-.08		-.01		-.06

Table 15

SHOWING PERCENTAGE DISTRIBUTION OF NITROGEN AT 600° C

	3		7		11		14	
	%	%distrib	%	%distrib	%	%distrib.	%	%distrib
Coke	2.23	96.12	1.47	94.53	1.54	96.25	1.61	94.16
Tar	.045	1.94	.057	3.65	.042	2.63	.064	3.74
NH ₃	.046	1.98	.028	1.79	.019	1.19	.035	2.04
Error				-.12		-.01		-.07

the different temperatures; Figures 9 to 10 the percentage of nitrogen in tar and ammonia at each temperature and Figures 11 to 13 the percentage distribution of nitrogen in coke, tar and ammonia at the respective temperatures.

A comparative study of these graphs is very useful and brings to light some very interesting facts regarding the constitution of coal. Thus in Figure 6 showing the quantities of tar given off, there is a decomposition of the coal at 450° (or slightly above) yielding a rapid evolution of tar. At 500° C most of the tar has been given off in all cases except that of No. 11, which continues gradually up to 550° C before a lag in the curve is observed. On the other hand in the case of ammonia (Fig. 7) the rapid evolution of ammonia only begins at 500° C. This again is true in all cases, except that of No. 11, when the rapid evolution only begins at 550° C. Thus in all cases it is shown conclusively that the molecule containing the bulk of the nitrogen only starts decomposing after all the tar has been removed. Furthermore this decomposition follows directly after the expulsion of the tar. A small portion of the nitrogen, however, comes off with the tar and is closely associated with it.

Furthermore it is seen that at 600° C these coals yield quantities of nitrogen as ammonia in direct proportion to the total quantity of original nitrogen in the coal. Thus in Figure 10 coal No. 3, containing the highest percentage of nitrogen liberates also the greatest amount of nitrogen as ammonia at 600° C. Coals No. 14, No. 7 and No. 11 follow in order. This, however, is not the case at lower temperatures. At 500° coal No. 11 liberates a greater amount of nitrogen than coal No. 7

and coal No. 7 more than coal No. 14. This is further evidence that this part of the nitrogen is distinct from the main portion of the nitrogen molecule. The behaviour of the nitrogen in the tar shows the same character (Fig. 9). Here again we find that even at 600° C coals Nos. 11 and 3 and coals Nos. 7 and 14 approach one another very closely in their percentages of nitrogen. In all cases the percentages of nitrogen in the tar approach a certain limit which does not differ to any extent with different coals.

Considering these results as a whole, though limited in scope and kind, we are led to believe that the nitrogen in coal exists in at least two forms--the one a less stable, and the other, which is by far the greater part, a very stable form. The less stable form comes over with the tar and is closely related to it. There is no evidence to show that the tar and the nitrogen belong to distinct molecules. On the contrary the general behaviour of the coals as shown by these graphs give strong indications that the tar and the nitrogen originate from different parts of the same molecule. /

Figures 11, 12, 13 show the percentage distribution of the nitrogen in the coke, tar and ammonia at different temperatures. These graphs throw some light on another property of the coal, namely its stability towards heat. Thus coal No. 14 distributes the greatest percentage of its nitrogen as ammonia and as tar at 600° C (Fig. 13). Coal No. 14, therefore, decomposes most rapidly after the temperature of decomposition is reached. Coal No. 3 on the other hand decomposes rapidly up to

550° but stops decomposing, as far as nitrogen is concerned, at this temperature, indicating greater stability of the nitrogen molecule. The decrease of the nitrogen distribution in the coke (Fig. 11) illustrates the point in question in a still more interesting way. In all cases except No. 3 the decrease is continuous. In the case of No. 3 the decomposition stops at 550° C. This temperature of greater stability is important and seems to be distinct for each coal. Probably at this temperature we get a decomposition of another kind leaving the nitrogen in a form which is not easily decomposed by heat. It is also possible, however, that the more stable form of nitrogen mentioned above, itself exists in two forms--the one more stable than the other.

It is further possible, and very likely, that we have here a case of polymerisation. The changes which take place follow one another in direct succession, which suggests such a state of affairs very strongly. Frans Fischer (49) believes that the humic acid present in the coal polymerises during the course of its formation to form humin. It is not unlikely that this same condition exists in the resinous part of the coal and that the intricate nature of all coals is due almost entirely to the degree of polymerisation of the compounds present.

Figure 8 shows the yield of gas given off at different temperatures. There are no sudden breaks in these curves. In fact the increase in gas is more or less gradual and consistent between these temperatures. It appears that the gas originates from a different part of the coal altogether, and for the sake of convenience we might look upon coal as being made up of two

Fig. 5 SHOWING AMOUNTS OF VOLATILE MATTER WITH TEMPERATURE

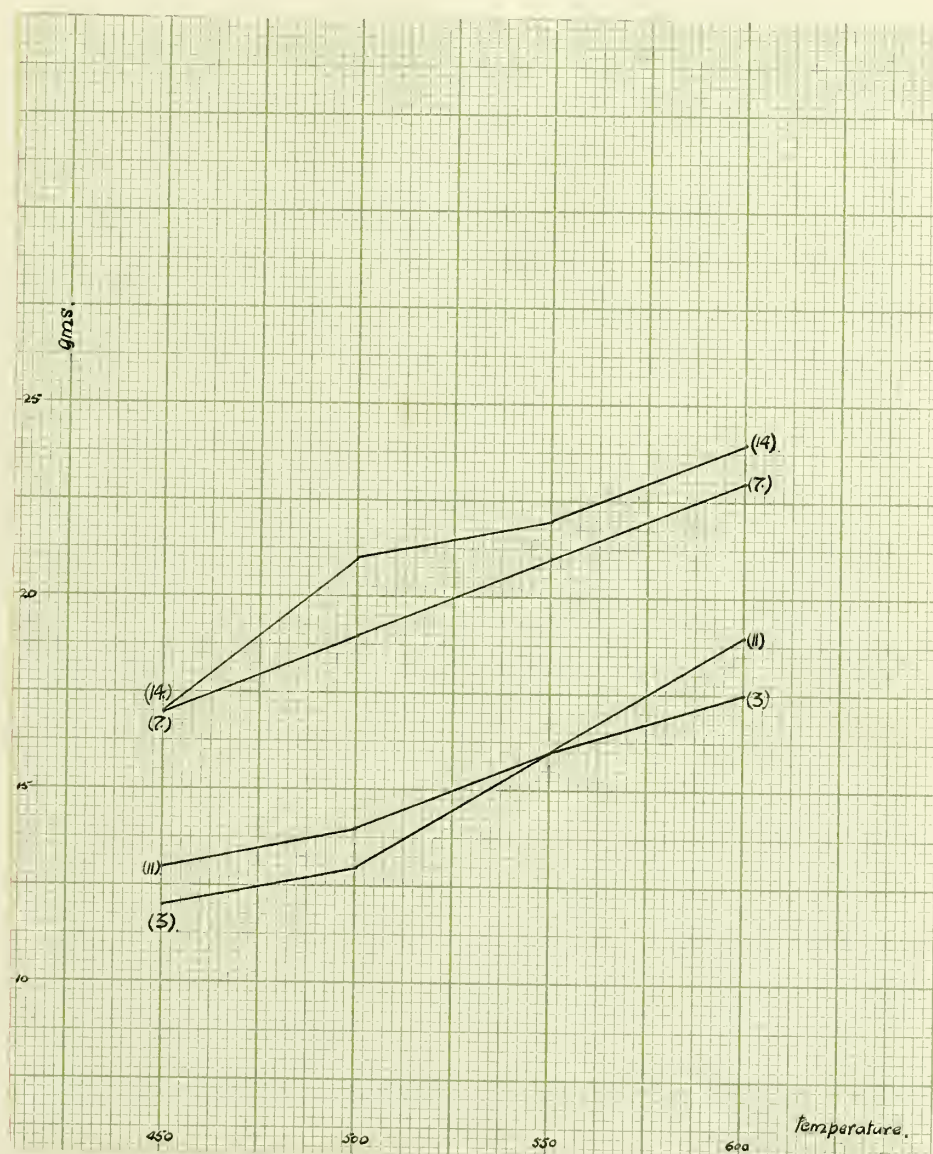


Fig.6 SHOWING AMOUNTS OF TAR GIVEN OFF BETWEEN 450° - 600°C

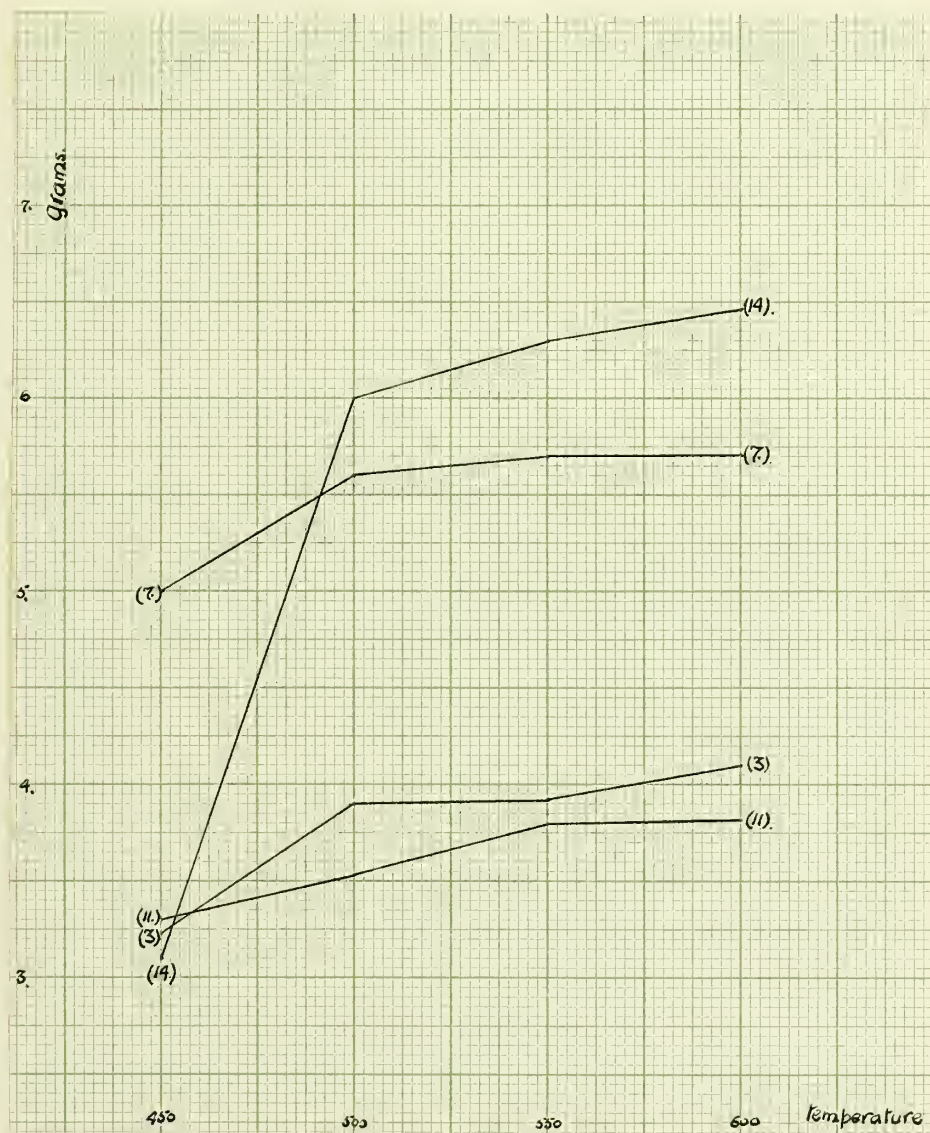


Fig. 7 SHOWING QUANTITIES OF AMMONIA GIVEN OFF BETWEEN 450°C-600°C

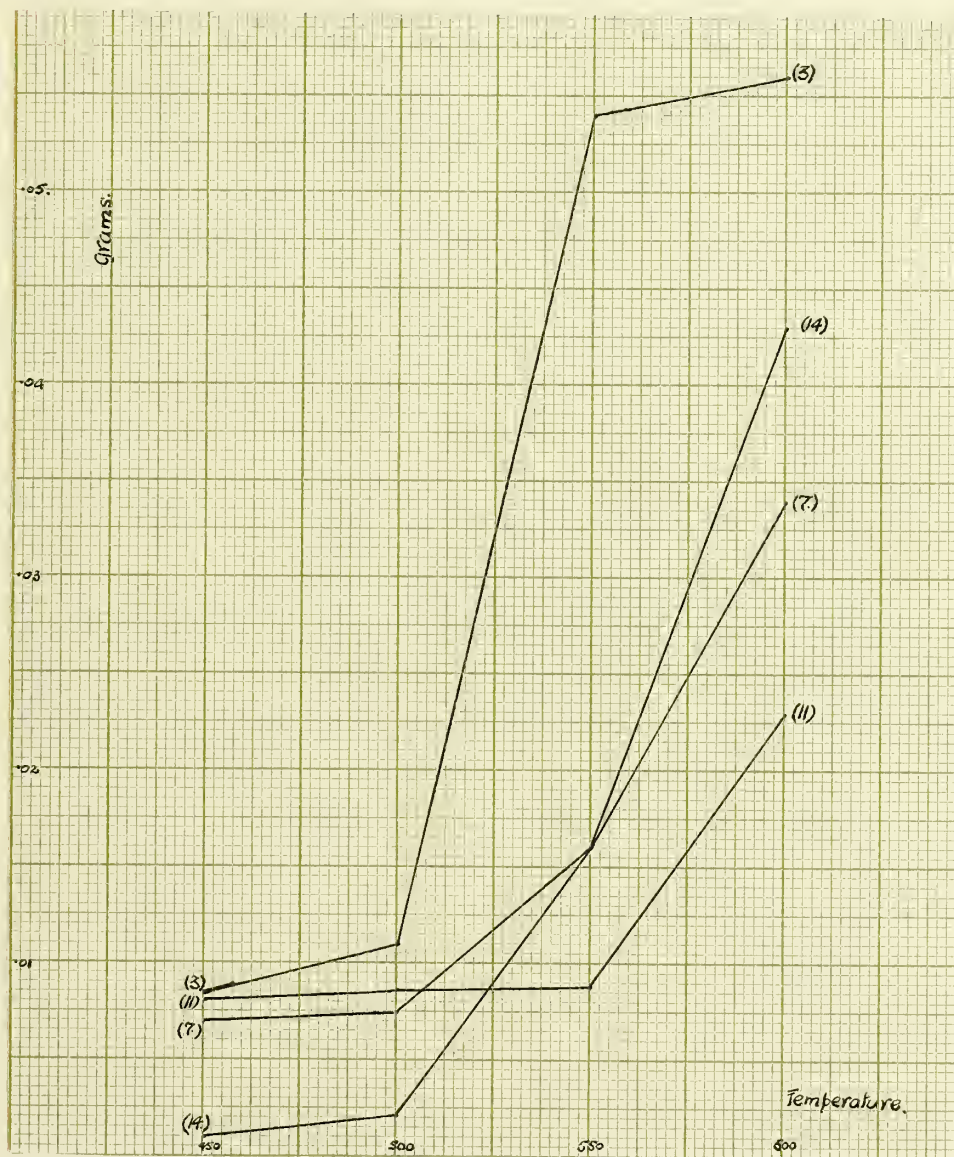


Fig. 8 SHOWING QUANTITIES OF GAS GIVEN OFF BETWEEN 450°-600°C

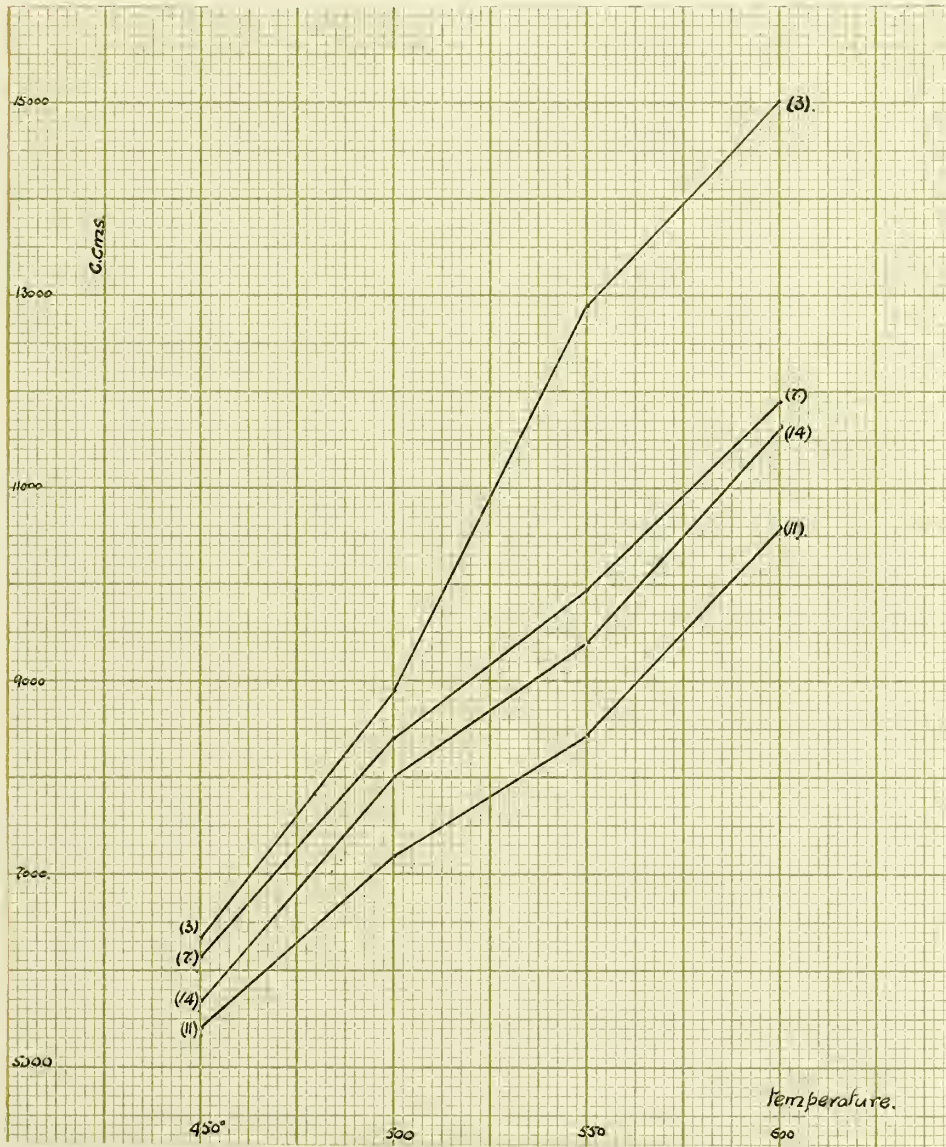


Fig. 9 SHOWING PERCENTAGE NITROGEN IN TAR BETWEEN 450°-600°C

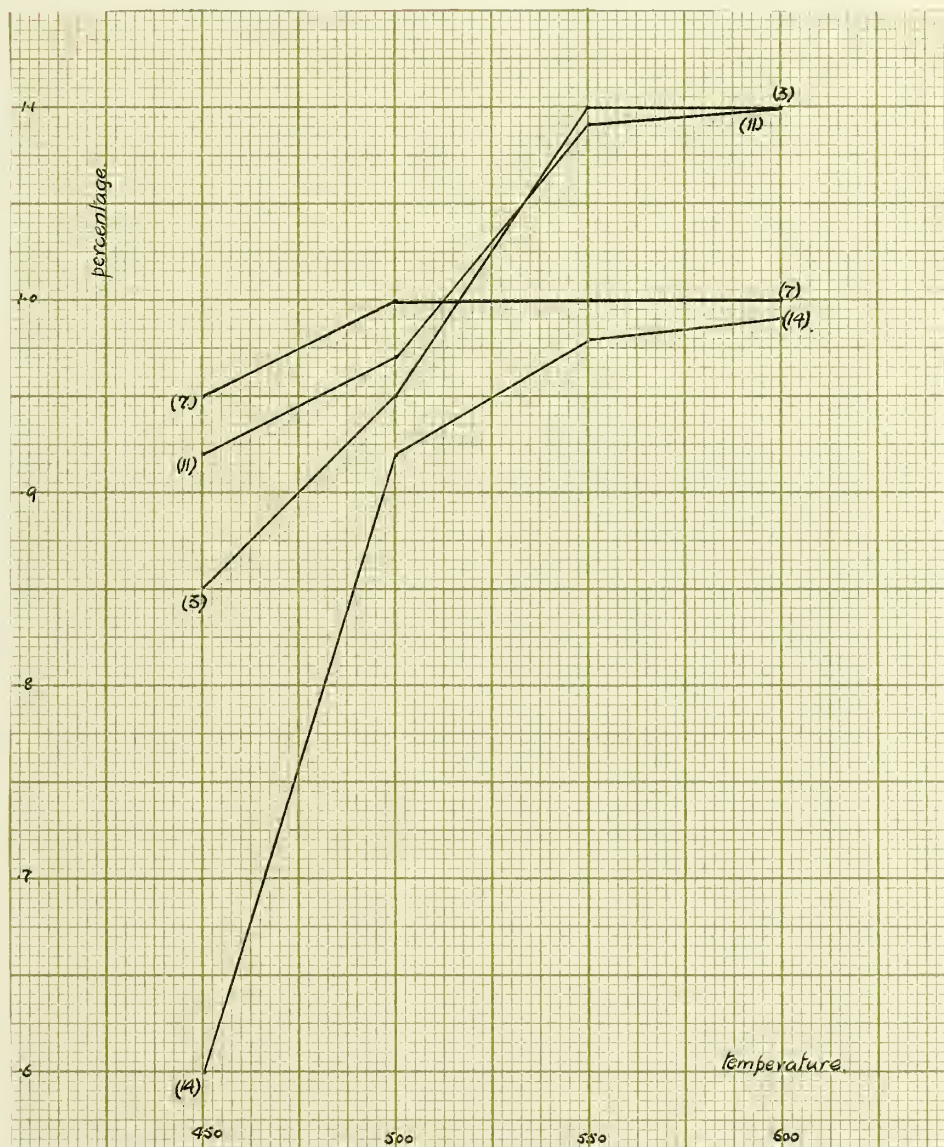


Fig. 10 SHOWING PERCENTAGE NITROGEN GIVEN OFF AS AMMONIA
BETWEEN 450°-600°C

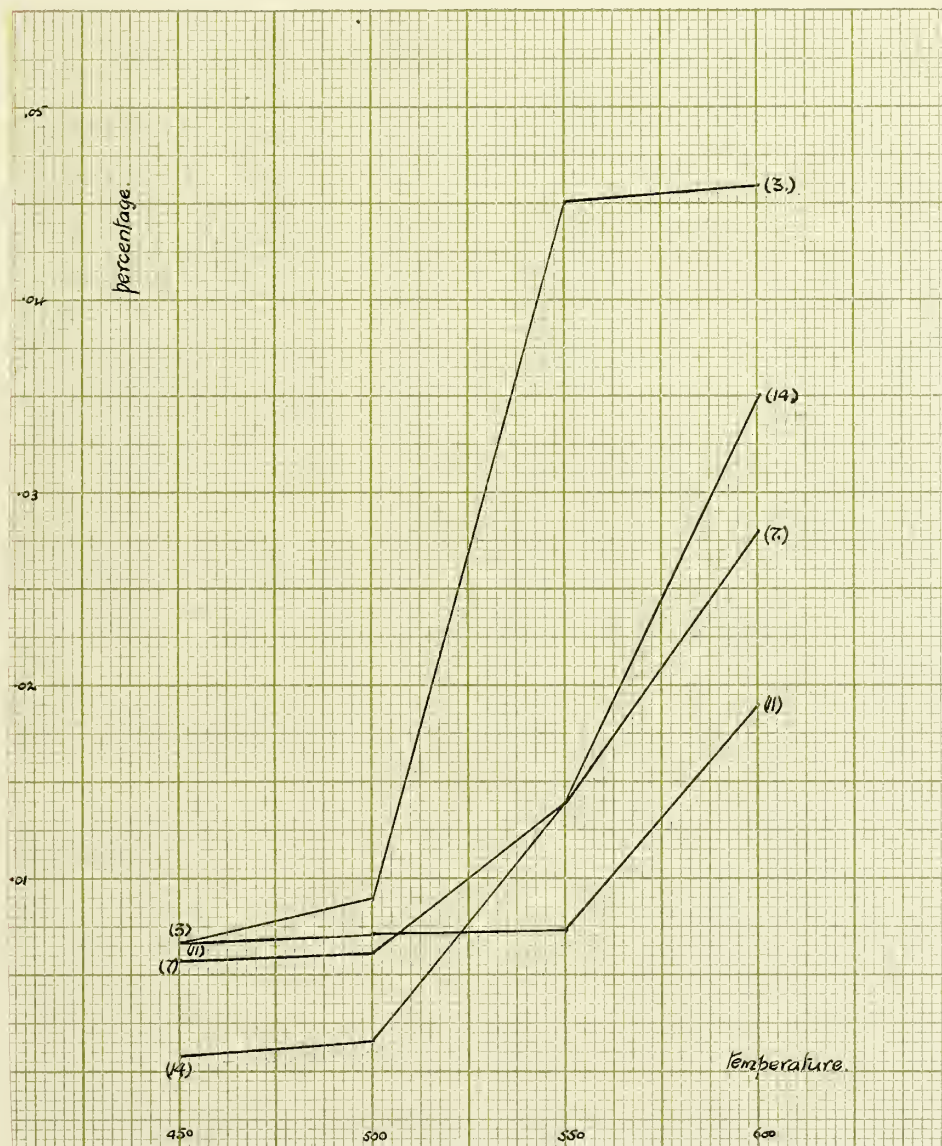


Fig. 11. SHOWING PERCENTAGE DISTRIBUTION OF NITROGEN IN COKE
BETWEEN 450°-600°C

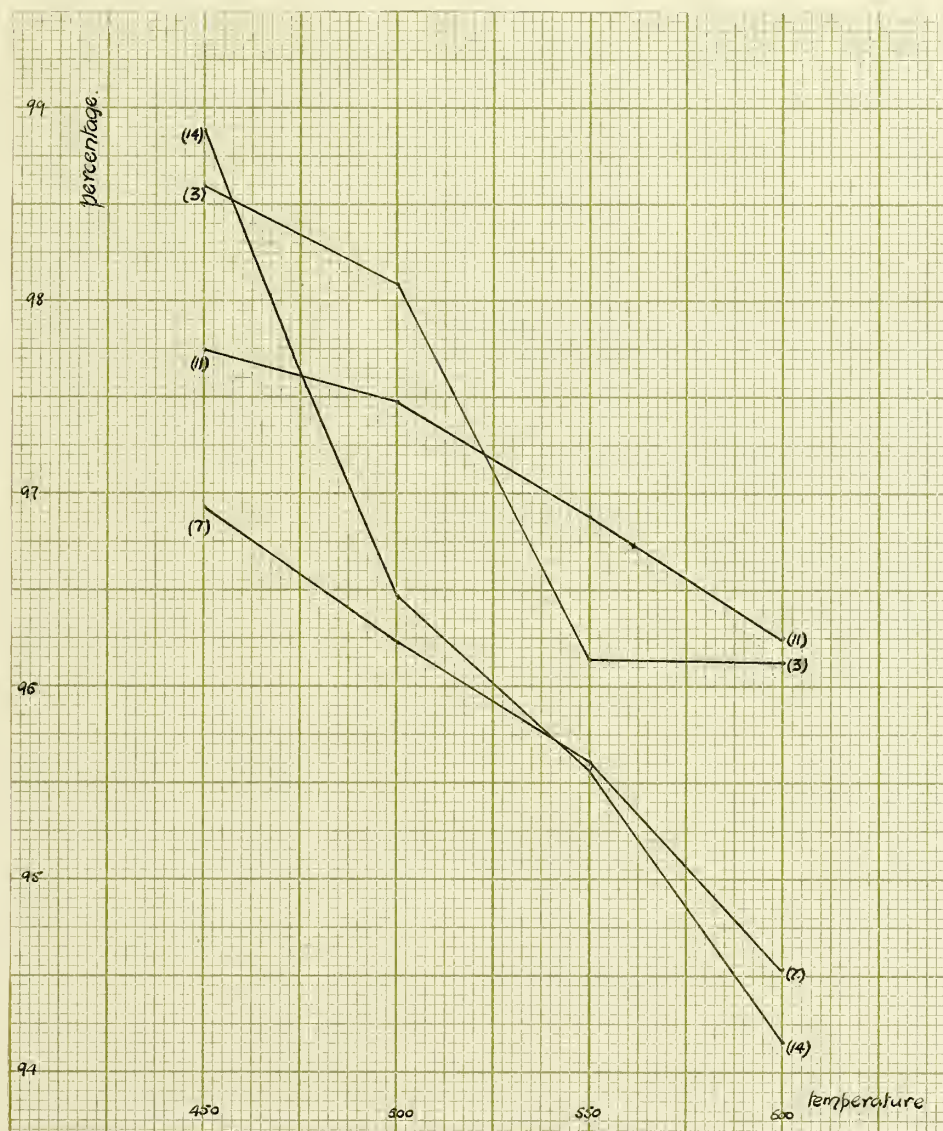


Fig. 12 SHOWING PERCENTAGE DISTRIBUTION OF NITROGEN IN TAR
BETWEEN 450°-600°C

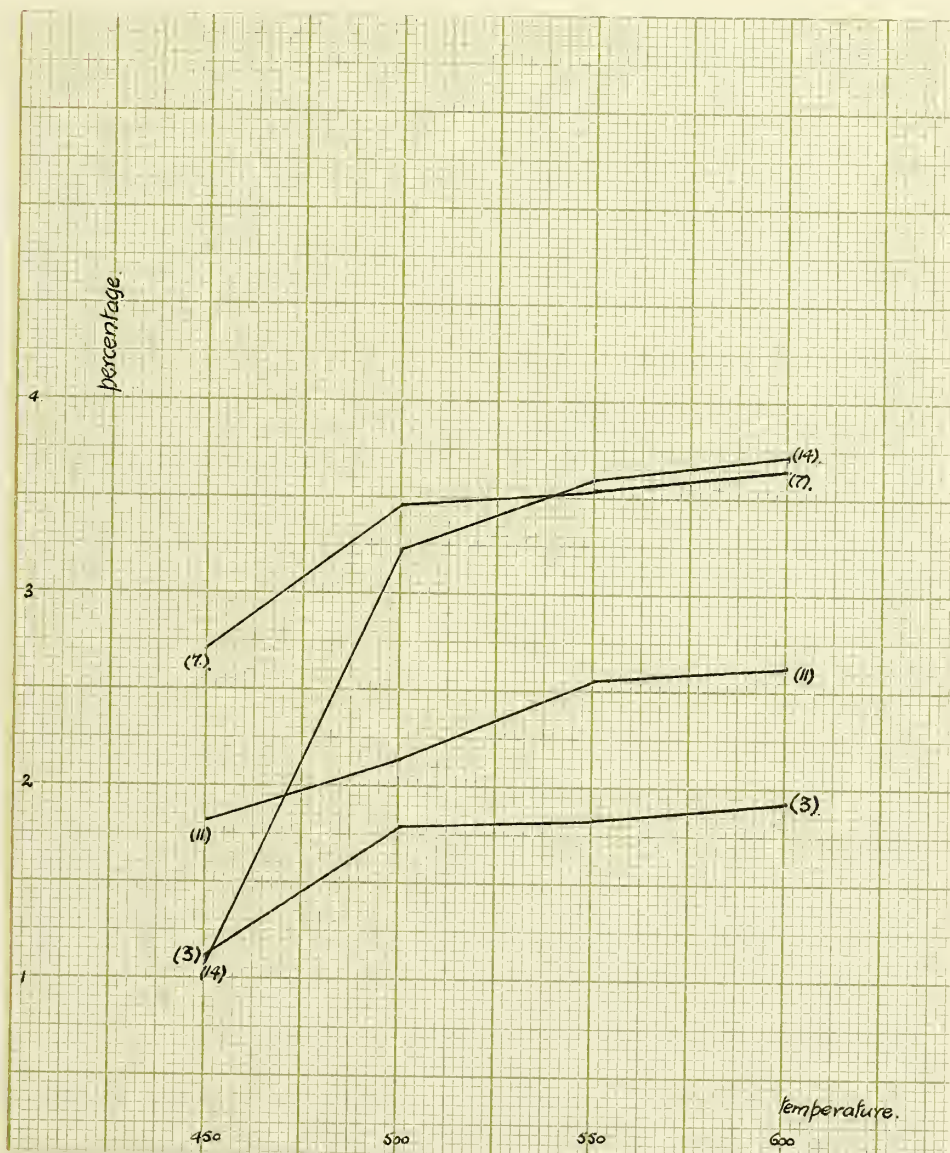
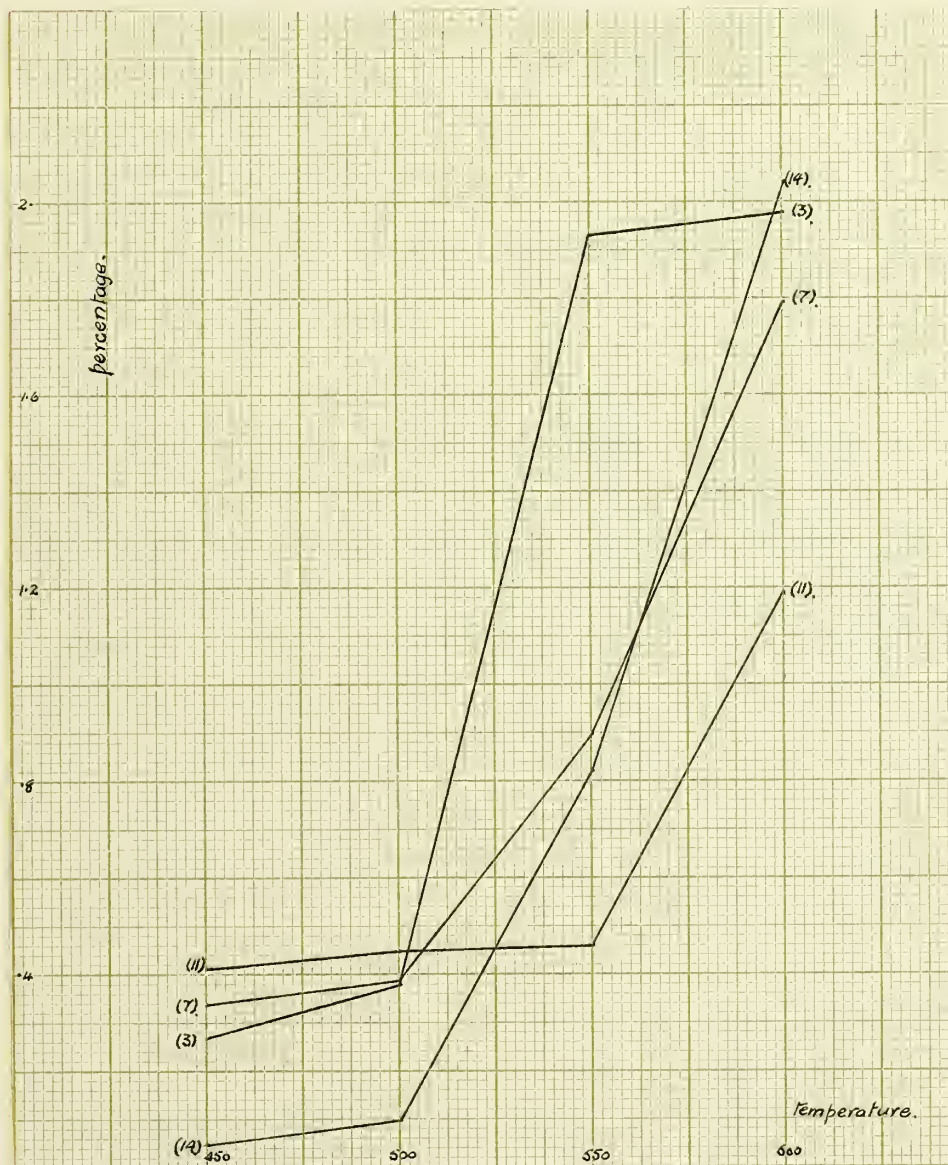


Fig. 13 SHOWING PERCENTAGE DISTRIBUTION OF NITROGEN
GIVEN OFF AS AMMONIA BETWEEN 450°-600°C



portions, (1) the gas producing and (2) the tar producing portion. By the gas producing portion is meant that portion of the coal which supplies the more useful gases such as hydrogen on the action of heat and is therefore equivalent to what is often called the "cellulosic" portion. The "tar producing" portion is that part of the coal which has resulted from the final combination of those substances originating from the resins and proteins in the plant. This line of division is not intended to be absolutely marked, but rather one of degree. It is evident that the hydrocarbons in gas originate from the tar producing portion of the coal. But in the main this part of the coal is not gas producing. The division is more exact than those previously suggested and is in agreement with the theory held by Taylor, Porter, Thiessen, Parr and others, that the cellulosic portion of coal is the first to decompose on heating, rather than that held by Wheeler and his co-workers, that the cellulosic or "hydrogen producing" part of the coal is the more stable to heat.

The Effect of Steam on Coke Residues

Following these results the effect of steam at 650°C and 750°C was tried on the coke residues obtained at 500°C and 600°C. The apparatus used is shown in Figure 14.

2 gms of coke were placed in the U tube D, made of pyrex glass. In each side of the tube is placed a plug of asbestos wool and finally small fireclay blocks about the size of a pea. Steam is generated in A, and at the same time the temper-

-ature of the furnace is raised until 650°C is reached. The gases are then passed through a condenser and into E containing standard $\frac{n}{10}$ sulphuric acid.

This process is continued for two and a half hours when the acid in E is renewed and the temperature raised to 750°C . The contents of E obtained at 650°C are now distilled and the amount of ammonia which was evolved calculated. At 750°C the reaction is carried on for $3\frac{1}{2}$ -4 hours until no more ammonia is evolved and the contents distilled as before. In this way an estimation is obtained of the exact amount of ammonia given off at these two temperatures in the presence of steam. By weighing the residue and analysing it for nitrogen we are able to calculate the distribution of nitrogen under these conditions. Tables 16,17 show the effect of steam on the coke residues at 650°C and 750°C and tables 18,19 the percentage distribution of nitrogen. The nitrogen which is listed as "unaccounted for nitrogen", in the tables is evidently free nitrogen arising from the dissociation of ammonia at this high temperature.

The percentage of the nitrogen liberated from the coke is in all cases low. At these temperatures it seems as though steam has little effect in liberating the nitrogen. In order to do this a higher temperature is evidently necessary so that the coke and steam may combine to form oxides of carbon, thereby leaving the nitrogen free to combine with the hydrogen to form the ammonia.

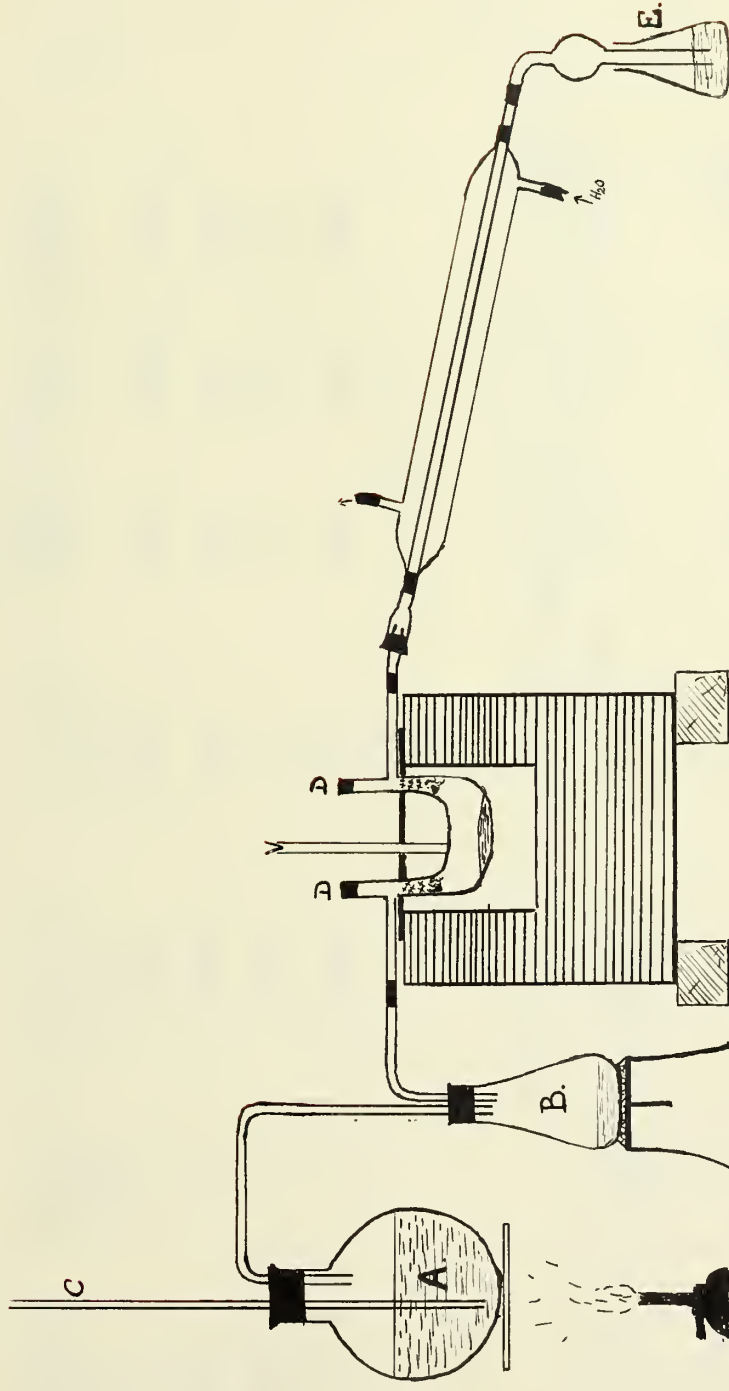


Fig. 14.— Apparatus , showing passage of steam over coke —

Table 16

EFFECT OF STEAM ON 500°C COKE

Coke	% nitrogen in coke	amount taken gms.	amount of residue gms.	% nitrogen in residue	% Nitrogen as Ammonia at		% N ₂ of the coke given off as NH ₃
					650°C	750°C total	
3 E	2.68	2	1.86	2.01	.148	.2324 .3804	14.18
7 F	1.89	2	1.725	1.52	.110	.24 .350	18.52
11 G	1.80	2	1.715	1.46	.119	.217 .336	18.67
14 H	2.07	2	1.726	1.73	.126	.217 .343	16.57

% N₂ of the
coke given off
as NH₃

Table 17

EFFECT OF STEAM ON 600°C COKE % Nitrogen as Ammonia at

Coke	% nitrogen in coke	amount taken gms.	amount of residue gms	% nitrogen in residue	% Nitrogen as Ammonia at		% N ₂ of the coke given off as NH ₃
					650°C	750°C total	
3 M	2.70	2	1.83	2.07	.112	.219 .331	12.26
7 N	1.91	2	1.79	1.54	.106	.177 .283	14.82
11 O	1.78	2	1.73	1.39	.0938	.171 .2648	14.88
14 P	2.12	2	1.745	1.74	.102	.186 .288	13.59

Table 18

DISTRIBUTION WITH 500°C COKE

Nitrogen	3 E	7 F	11 G	14 H
as Ammonia	14.18	18.52	18.67	16.57
remaining behind in coke resi- due	69.38	69.34	69.56	72.12
Unaccounted for	16.44	12.14	11.77	11.31

Table 19

DISTRIBUTION WITH 600°C COKE

Nitrogen	3 M	7 N	11 O	14 P
as Ammonia	12.26	14.82	14.88	13.59
remaining in coke residue	70.01	69.34	70.01	71.61
Unaccounted for	17.73	15.84	15.11	14.80

B. Chemical Reagents

In the series of experiments just described it is evident that the nitrogen molecule constitutes the tar producing portion of the coal, and that the structure of this molecule, in one respect, constitutes the structure of coal. In the experiments which are to follow attempts are made to isolate the nitrogen molecule or break it up by the action of chemical reagents in such a way that it may be recognised in its original form in the coal.

According to the theoretical considerations described above it is evident that, after hydrolysis of protein has taken place, several reactions may again take place amongst the products of decomposition. All of these products being acids, they may act as such on other organic compounds in the plant to form open chain derivatives, or ring compounds of a more stable nature. On the other hand they may remain in the coal as such in a highly polymerised form or they may decompose altogether and pass off in the form of N_2 and ammonia in the secondary stages of coal formation.

In order to get some idea of any such secondary changes which may have taken place, certain chemical reactions were tried on the coal, keeping the temperature in all cases as low as possible.

In the first series of reactions the effect of hydrolysing agents was tried on the coal.

Hydrolysing Agents

In all these reactions preference was given to the method of examining the residue for nitrogen rather than the ex-

tract. In each case the percentage of nitrogen in the residue was determined and calculated to the ash and moisture free basis. Thus by comparing this figure with the original percentage of nitrogen in the coal, calculated on the moisture and ash free basis a satisfactory indication of the extent to which the nitrogen molecule was affected can be obtained. The following hydrolysing agents were tried.

a. Two different strengths of hydrochloric acid were used, namely a 12% and a 40 % solution. 50 gms of coal were heated under a reflux condenser for 10 hours with an excess of these solutions. The residue was washed until the wash water is free from acid and the air dried and analysed.

b. N. Zelinsky (54), preferred using formic acid for hydrolysing purposes, so that in these experiments a 25 % solution of formic acid was tried as well.

c. Aqueous Potassium Hydroxide was tried in three different strengths 1, 5 % ; 2, 10 %; 3, 30 %. The residues were washed to give no coloration with phenolphthaleine, air dried and analysed. The extracts were coloured brownish red, the intensity of the colour increasing with the strength of the solution of potassium hydroxide used. The extract, on treatment with HCl gave a white gelatinous precipitate soluble in excess. The same precipitate was produced with all other common acids. In excess quantities of alcohol the precipitate was insoluble and was separated in this way from the extract. It was found to be aluminum oxide. The solution was finally evaporated to a small bulk and tested for nitrogen with negative results.

a. A 10 % alcoholic potash solution was used in a similar way

(1) at the ordinary pressure and (2) at 3 atmospheres pressure.

Table 20 shows the results obtained in these reactions. In all these cases a certain amount of resinous bodies are extracted from the coal, together with quantities of alumina and iron. The table clearly indicates that the main part of the nitrogen molecule remains unaffected. It is also evident that a very small portion of the nitrogen has been removed.

If the reagent attacks only the ash of the coal, then the ash content would be lowered and the nitrogen content correspondingly raised, and the percentage of nitrogen on the moisture and ash free basis would not be altered. But if the volatile matter in addition is attacked so as to remove some of it, then the ash and nitrogen content would be raised and the percentage of nitrogen calculated on the moisture and ash free basis would be higher. In all cases a certain amount of the volatile matter is removed. It is, therefore, seen that all of the above reactions have had a small effect on the nitrogen content of the coal.

An attempt was then made to determine quantitatively the amount of nitrogen that was removed in the above reactions. This nitrogen we would expect to be in the form of acid amides and amino acids, and in order to determine their amounts quantitatively the following methods were employed.

20 gms of coal are placed in a one litre round bottom flask and heated under reflux for 3-4 hours with 300CC of hydrochloric acid (1.1). The mass is then filtered under suction and the residue washed with hot water. The solution is evaporated down to a small bulk, transferred to a measuring flask and made up to 100 CC. 50CC of this amount was kjeldahlized to give the total

Table 20

SHOWING EFFECT OF HYDROLYSING AGENTS ON THE NITROGEN CONTENT

Treatment	Experiment Number	Time of extract	H ₂ O	Asn	N ₂	N ₂ Moisture & Asn free basis	N ₂ in coal moisture, as free basis
12 % Hydrochloric Acid	4 a	10 hrs.	1.06	7.28	2.16	2.36	2.26
40 % Hydrochloric	8 a	14 hrs.	2.09	12.60	1.61	1.89	1.86
25 % Formic Acid	14 a	14 hrs.	2.20	10.15	1.80	2.05	2.05
5 % Potassium Hydroxide	14 b	8 hrs.	2.24	10.13	1.82	2.08	2.05
10 % Potassium Hydroxide	14 c	8 hrs.	2.54	9.67	1.80	2.05	2.05
30 % Potassium Hydroxide	14 d	8 hrs.	4.66	10.26	1.76	2.07	2.05
10% Alcoholic KOH	14 e	8 hrs.	6.29	10.59	1.75	2.10	2.05
25 % Potassium Hydroxide 125°C & 3 atm. pressure	14 f	4 hrs.	2.93	11.04	1.83	2.13	2.05
10 % Alcoholic KOH 110°C & 3 atm.	14 g	4 hrs.	2.88	11.32	1.79	2.04	2.05

amount of amido and amino nitrogen present. The remaining 50 C C of this amount were used to determine the amido nitrogen, by distilling a known quantity in the presence of cream of magnesia. The amido nitrogen alone distills over as ammonia which is collected in standard acid. The difference in the two results gives the amount of amino nitrogen present.

All fourteen samples of coal were treated in this way and the results tabulated (table 21). It is seen that the amount of amido nitrogen is in almost all cases greater than the amount of amino nitrogen. This is what we would expect, if results obtained by Kelley (55) on the rate of ammonification of these forms of nitrogen can be applied in this case. Kelley added protein substances to quartz sand, previously treated with soil infusion and studied the rate of ammonification. He found, contrary to expectation, that the basic nitrogen fraction was more completely ammonified than either the amido or non-basic fraction. Lathrop a little later (56) came to similar conclusions.

The amounts of amido and amino nitrogen present in the coal are surprisingly low and in order to be able to come to definite conclusions regarding this matter, an attempt was made to remove all NH_2 groupings in another way.

When carbonyl chloride is passed over heated amines a carbamic chloride is formed, which readily loses HCl to form an isocyanate.

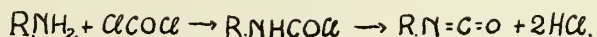


Table 21

SHOWING PERCENTAGE OF NITROGEN PRESENT AS AMIDES
AND AMINO ACIDS

Coal	Nitrogen as Amides	Nitrogen as Amino Acids	Total "NH ₂ " Nitrogen	% of Total N ₂
1	.0078	.0048	.0122	.57
2	.010	.0076	.0176	.81
3	.0336	.0026	.0362	1.56
4	.020	.0094	.0294	1.35
5	.0125	.0127	.0252	1.50
6	.0124	.0125	.0249	1.54
7	.0112	.0042	.0154	.92
8	.0155	.0069	.0224	1.46
9	.0140	.0082	.0222	1.33
10	.0309	.0030	.0339	1.60
11	.0175	.014	.0184	1.14
12	.020	.0045	.0265	1.53
13	.0186	.0071	.0257	1.47
14	.010	.007	.0170	.95

The isocyanic esters are volatile liquids with a powerful unpleasant smell.

If coal contains amino groupings then, when COCl_2 is passed over it at higher temperatures, we should expect the corresponding nitrogen compounds to volatilize.

100 gms of previously dried coal were placed in a long tube furnace, which was electrically heated. The temperature was controlled by means of a thermometer placed at each end. The COCl_2 was purified by passing it through cotton seed oil and finally over the coal at 250°C and 350°C . The results given in the case of two coals show conclusively that very little action took place. (Table 22)

Table 22 SHOWING EFFECT OF CARBONYL CHLORIDE

<u>Treatment</u>	<u>Expt. No.</u>	<u>H₂O</u>	<u>Ash</u>	<u>N₂</u>	<u>H₂O & Ash free basis N₂</u>	<u>Ong. N₂ H₂O & Ash free</u>
250°	14 ₁	1.38	11.37	1.90	2.18	2.05
350°	14	1.36	11.83	1.89	2.19	2.05
350°	3 ₁ ²	1.45	7.11	2.35	2.57	2.55

We are now in a better position to formulate our theory as to the changes which the protein molecule undergo during the different stages of coal formation. The monamino, diamino acids and acid amides which come into the mass as decomposition products of the protein molecule, are no longer present to any extent in the coal. Consequently these compounds, either combined with themselves or with other organic compounds to form more stable ring derivatives, or they are decomposed and pass off from the

mass in the form of ammonia or nitrogen , thus leaving the heterocyclic compounds, which are present in proteins, to form the bulk of the nitrogen found in coal. It is an established fact that amino acids and acid amides will readily ammonify in the presence of bacteria in the soil. We are, therefore, more entitled to assume such a state of affairs in the case of coal than we are to assume ~~such~~ a state of further combination. The conditions during coal formation are favorable for such decompositions. The fact that all coals from the same locality contain amounts of nitrogen which are more or less constant, further suggests a compound which is stable to the natural agencies to which it is exposed. The heterocyclic compounds are the only portions of the protein molecules that will satisfy this condition. If this is the case then in order to account for some of the properties of coal, we must assume that these compounds have undergone polymerization to a great and unknown extent.

Selenium Oxychloride

According to researches done by Prof. Lenher of the University of Wisconsin, Selenium oxychloride is a very useful and active selective solvent. Its effect was therefore, tried on coal as an attempt to separate the stable nitrogen molecule.

Five grammes of coal No.3 and 25 CC of pure selenium oxychloride were placed in a conical flask and corked. The mixture is warmed and shaken continually for 1/4 hour, when the extraction is assumed to be complete. In order to get this solution to filter so as to separate the residue from the extract

the mixture is diluted with 200 C C of benzene. Filtering under suction is thus rendered possible. The residue is now washed well with benzene to remove as far as possible any adhering SeOCl_2 then with ether and finally dried at 105°C .

The extract when heated with water deposits red selenium. When benzene alone is mixed with selenium oxychloride in these proportions and water added to the mixture, the selenium oxychloride hydrolyses to selenic and hydrochloric acids without any deposit of the element. Thus when selenium oxychloride acts on coal a chemical reaction is assumed to take place and a compound is formed which readily deposits selenium.

The extract was treated with excess of sodium hydroxide and steam distilled. Finally it was vacuum distilled but no nitrogen compounds were found.

The residue was analysed for nitrogen and results calculated to the moisture and ash free basis. Finally for purposes of comparison the action of selenium oxychloride was tried on 500°C coke obtained in previous experiments (see table 9). This coke had practically all its tar already removed. The reaction was significant. Hardly any result could be seen, except a coloration of the solution, showing that the selenium oxychloride reacted with the tar in the coal. The mass was easily filtered and the residue washed with benzene and ether and finally analysed. The results are given in table 23.

Table 23 SHOWING ACTION OF SELENIUM OXYCHLORIDE

<u>Treatment</u>	<u>Expt.</u>	<u>H₂O</u>	<u>Ash</u>	<u>N₂</u>	<u>Orig. N₂</u>
				<u>H₂O, Ash free</u>	<u>H₂O, Ash free</u>
Coal & SeOCl_2	32	-	6.23	1.79	2.55

Table 23 SHOWING ACTION OF SELENIUM OXYCHLORIDE

<u>Treatment</u>	<u>Expt.</u>	<u>H₂O</u>	<u>Ash</u>	<u>N₂</u>	<u>N₂</u> <u>H₂O, Ash free</u>	<u>Orig. N₂</u> <u>H₂O, Ash free</u>
Coal & SeOCl ₂ (residue)	3'	-	6.23	1.79	1.91	2.55
Coke & SeOCl ₂ (residue)	3''	2.07	7.94	2.65	2.94	2.96
or original coke 550°C (3E)	3'''	.54	9.14	2.68	2.96	2.96

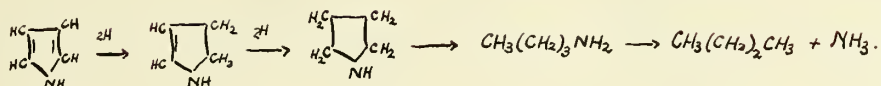
From these figures it appears that the nitrogen in the coke remains unaffected. In the case of the coal it would appear as though some of the nitrogen was removed. Selenium oxychloride on the other hand is extremely active and forms a compound with the coal, so that it is impossible to rid the residue of the reagent. This is seen very forcibly by the result obtained in a volatile matter determination on the residue. It was found that the volatile/matter on treatment with SeOCl₂ increased in the case of coal NO₃ from 23.10 % to 31.34 %. Taking these figures into account the two results coincide showing conclusively that selenium oxychloride will not attack the stable part of the nitrogen molecule.

The Action of Reducing Agents

Subsequent to these results the coal was subjected to the action of reducing agents in order to observe what effect hydrogenation would have on the nitrogen molecule.

When pyrrol is reduced pyrroline is obtained. With strong reducing agents, such as red phosphorus and hydriodic acid pyrroline is further reduced to alkylamine or still further to

hydrocarbon and ammonia as is illustrated by the following formulas:



If the nitrogen in coal is present in the form of pyrrol derivatives, as we have been led to believe, then strong reducing agents should have some effect on the nitrogen molecule. In order to try out this reaction propyl alcohol and sodium, and red phosphorus and hydriodic acid were used as reducing agents.

(a) Propyl Alcohol and Sodium

20 gms of coal were placed in a two litre round bottom flask containing a reflux condenser and 500 gms of propyl alcohol added. The mixture is warmed to boiling and small pieces of sodium added. The flask is shaken continually so that the contents are kept mixed all the time. When no more sodium reacts sufficient water is added to decompose any free sodium. At this stage the coal assumes the appearance of a soft, oily resinous mass, which floats on the surface of the liquid. The mixture is cooled, filtered washed and air dried. But while being air dried the coal seems to undergo oxidation again and is converted back into its original appearance. Table 24 shows its analysis on the moisture and ash free basis. Evidently very little nitrogen was removed in this case.

(b) Hydriodic acid and Red phosphorus

The reaction with hydriodic acid and red phosphorus at higher temperatures is more difficult to carry out successfully owing to the enormous pressure set up during the reaction. A mercury container with a specially designed screw cap was used.

At 200°C the reaction was carried out successfully but at higher temperatures the container failed to withstand the pressure entirely and leaked through the cap. For this reason experiment (14C) could not be run satisfactorily, though a certain measure of success is evident from the amount of nitrogen that was removed in the process.

50 gms of coal were mixed with 10 gms of red phosphorus and 350 gms of hydrogen iodide of 50 % strength. The mixture was heated for two hours (a) between 180-200°C and (b) 250°-280°C. On cooling and filtering the residue and extract in the latter case were treated as follows:

(1) Treatment of residue;

The residue was treated with iodine and water and boiled for a short time to remove any excess phosphorus. The phosphorus and iodine combine to form PI_3 , which is decomposed by water, forming phosphoric acid which is soluble and hydrogen iodide which passes off as a gas. The excess of iodine is removed by washing with a strong solution of potassium iodide and finally with water to remove the latter. Finally it is air dried and analysed. (Table 24)

(2) Treatment of the Extract

The extract was a green color. On diluting it with water a brilliant yellow precipitate settles out. This precipitate contained carbon, hydrogen, oxygen and iodine. On boiling with water it hydrolyses to a white insoluble substance containing the first three elements mentioned above. As the precipitate contained no nitrogen it was not investigated

any further.

On removing this precipitate, however, the solution was steam distilled in the presence of sodium hydroxide.. The steam distillate had a distinct ammoniacal smell and gave a dense precipitate with Nessler's reagent. No amimes could be detected with benzene sulphonyl chloride. Table 24 (exp. 14C) shows that quite a large proportion of the nitrogen was removed in this process.

Table 24 SHOWING EFFECT OF REDUCING AGENTS

<u>Treatment</u>	<u>Expt.</u>	<u>H₂O</u>	<u>Ash</u>	<u>N₂</u>	<u>N₂free H₂O & Ash basis</u>	<u>Orig N₂free H₂O & Ash basis</u>
Na & C ₃ H ₇ OH	14 A	3.29	10.52	1.69	1.98	2.05
HI & Phos. 180-200	14 B	1.44	14.10	1.67	1.98	2.05
HI & phos. 250-280	14 C	1.16	30.26	1.04	1.52	2.05

In these results we have further indications of the presence of pyrrol derivatives in coal. The fact that such a high temperature and pressure is necessary in the reaction further suggests polymenzation of these compounds.

SUMMARY ON THE FORM OF NITROGEN IN COAL

The experimental data arrived at in this work indicates certain theories regarding the constitution of coal and the form in which the nitrogen exists. All past theories on coal take into account cellulosic and resinic decomposition products and state that coal is made up of these two portions alone. This work shows conclusively that the nitrogen, or the decomposition products of protein cannot be neglected. The nitrogen molecule is closely related to the resinic portion of coal, and forms different parts of the same molecule from which the tar originates.

Two main forms of nitrogen have been established in this work; 1: NH_2 form, present as amino acids and acid amides, and; 2: a more stable form, probably in the form of a pyrrol ring which has undergone polymerisation. The NH_2 form does not constitute more than 1.6% of the nitrogen in the coals studied. As amino acids and acid amides readily undergo ammonification in the presence of bacteria, it is quite probable that they decompose and pass off from the coal mass during the period of formation. The heterocyclic compounds, which are present in proteins in the form of pyrrol rings, on the other hand, remain behind and account for the more or less constant percentage of nitrogen in all coals from the same locality. The pyrrol derivations undergo polymerisation to an unknown degree in the presence of the organic acids in the vegetal matter, and combine with the products of

decomposition arising from the resinic matter in plants. These products of decomposition are thus present in the form of long side chains attached to the polymerised pyrrol ring. The author would suggest that this compound be called the "tar producing portion" of the coal.

When coal is heated these side chains split off and distil over in the form of tar. The NH_2 nitrogen comes off with the tar and quite probably is present in these side chains. This accounts for the small percentage of ammonia given off at low temperatures. When practically all of the tar has been split off, the polymerised pyrrol derivative starts decomposing in stages and liberates ammonia and hydrocarbons. This accounts for the ^{relatively} small percentage of hydrocarbons found in gas. In this case acetylene will evidently be formed. Part of this acetylene combines with hydrogen to form ethylene and methane, and a further portion polymerises to form benzene, if the conditions are favorable. Finally a stage is reached where the polymerised compound is unsaturated and at the same time unstable. At this temperature the ring breaks and a compound remains in which nitrogen is probably combined directly with carbon. When this stage has been reached the ~~best~~ way to obtain the nitrogen in the form of ammonia, is by burning away the carbon in the presence of steam.

On these lines the presence of pyrrol and pyridine in coal tar can be explained, since it is a distinct property of five membered heterocyclic compounds containing nitrogen to be converted into six membered ring compounds. Pyrrol derivat-

ives furthermore readily polymerise in the presence of acids and these polymerised products decompose on heating to yield ammonia. The fact that polymerised pyrrol derivatives are unstable at higher temperatures indicates that the degree and kind of polymerisation which takes place during the stages of coal formation is yet unknown.

In regard to the actual behavior of the nitrogen in the coals studied, the following conclusions are drawn:-

- 1:- In distillation experiments carried out between 450 degrees and 600 degrees C the percentage of the nitrogen remaining behind in the coke is distinct for each coal and is independent of the total amount of nitrogen in the coal. As much as 98.85% of the nitrogen remains in the coal at 450 degrees C in one case. In this instance only .05% of the nitrogen is liberated as ammonia. At 600 degrees C an average of 95% of the nitrogen remains in the coal and not more than 2.04% of the nitrogen is liberated as ammonia. On further heating to 750 degrees C in the presence of steam an average of 70% of the nitrogen remains in the coke.
- 2:- Hydrolysing agents will affect the NH_2 nitrogen in the coal, but not the more stable form.
- 3:- In the coals studied the percentage of NH_2 -nitrogen varied from .57% to 1.60% of the total nitrogen present. In almost all cases the greater part of this nitrogen was in the amido form.

4:- Selenium oxychloride will react with the tar in coal and form a colloidal mass with it. It does not attack the stable form of nitrogen.

5:- Strong reducing agents will attack the nitrogen in coal to yield ammonia. Thus red phosphorus and Hydriodic acid at 250 degrees to 280 degrees reduces the percentage of nitrogen from 2.05% to 1.5%, calculated on the moisture and ash free basis.

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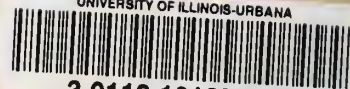
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